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Forum for CSIR-UGC JRF/NET, GATE, IIT-JAM/IISc, JEST, TIFR and GRE in PHYSICS & PHYSICAL SCIENCES

Kinetic theory, Thermodynamics

(IIT-JAM/JEST/TIFR/M.Sc Entrance)

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Thermal & Statistical Mechanics

1. Kinetic theory of gases……..(1-29)

1.1 Basic assumption of kinetic theory

1.1.1 Pressure exerted by a gas

1.2 Gas Law for Ideal gases:

1.2.1 Boyle's Law

1.2.2 Charle's Law

1.2.3 Avogadro's Law

1.2.4 Graham's Law of Diffusion

1.2.5 Ideal Gas Equation:

1.3 Kinetic Interpretation of Temperature

1.4 Maxwell-Boltzmann Distribution Law

1.4.1 The Distribution in term of Magnitude

1.4.2 To Determine Value of β in term of Temperature T

1.4.2 Average Velocity

1.4.3 Root Mean Square Velocity

1.4.4 Most Probable Velocity

Questions and Solutions

2. Real Gases…….(30-43)

2.1 Andrew's Experiment on Carbon Dioxide

2.2 van der Waals Equation of State.

2.3 Correction in Ideal Gas Equation to Achieve van der Waals Gas Equation of State.

2.3.1 Correction for Finite Size

2.3.2 Correction for Intermolecular Attraction

2.3.3 Maxwell Equal Area

2.3.4 Critical Point

2.3.5 van der Waals Equation of State and Virial Coefficient

Questions and Solutions

3. Basics of Thermodynamics and Laws of Thermodynamics……(44-79)

3.1 Mathematical Formulations of thermodynamics.

3.1.1 Some important Formulas

3.2 Fundamental Concept

3.2.1 System

3.2.2 Isolated System

3.2.3 Thermodynamical State

3.2.4 State Function

3.2.5 Intensive and Extensive Properties

3.3 The Ideal Gas:

3.4 Laws of Thermodynamics

3.4.1 Zeroth law of Thermodynamics:

3.4.2 First law of Thermodynamics:

3.4.3 Work Done during Different Process.

3.4.4 Specific Heat

3.4.5 Heat Capacity of Ideal Gas:

3.4.6 Molar Heat Capacity

3.4.7 Coefficient of Volume Expansion or Expansivity

3.4.8 Isothermal Elasticity and Isothermal Compressibility

3.5 Different Types of Thermo Dynamical Process and use of First Law of Thermodynamics

3.5.1 Isochoric Process:

3.5.2 Isobaric Process

3.5.3 Isothermal Process

3.5.4 Adiabatic Process

Questions and Solutions

4. Second Law of Thermodynamics and Entropy……...(80-110)

4.1 Second Law of Thermodynamics

4.2 Heat Engines

4.2.1 Heat Reservoir

4.2.2 Efficiency of Heat Engine (η)

4.2.3 Carnot Cycle

4.3 Entropy

4.3.1 Inequality of Clausius

Questions and Solutions

5. Maxwell relation and Thermodynamic Potential……..(111-142)

5.1 Maxwell relations

5.2 Different types of thermodynamic potential and Maxwell relation

5.2.1 Internal Energy

5.2.2 Enthalpy

5.2.3 Helmholtz Free Energy

5.2.4 Gibbs Energy

5.3 Application of Maxwell Relation

5.3.1 First $T - dS$ Equation

5.3.2 Second $T - dS$ Equation

5.3.3 Third T-dS Equation:

5.3.4 First Energy Equation

5.3.5 Second Energy Equation

Questions and Solutions

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6. Phase Transition and Low Temperature Physics……...(143-167)

6.1 Third Law of Thermodynamics and Attainable of Low Temperature

6.2 Production of Low Temperature and Joule – Kelvin Expansion:

6.3 Phase Transition

6.3.1 First Order Phase Transition

6.3.2 Equilibrium Between Two Phases

6.3.3 Clapeyron-Clausius Equation

6.3.4 Liquid-Vapour Phase Transition

6.3.5 Properties of First Order Phase Transition

6.3.6 Second Order Phase Transition:

Questions and Solutions

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Chapter - 1

Kinetic Theory of Gases

1.1 Basic Assumption of Kinetic Theory:

1. Any infinitely small volume of a gas contains a large number of molecule.
2. A gas is made up identical molecule which behaves as rigid, perfectly elastic, hard sphere.
3. The molecules continuously move about in random directions. All directions of motion are equally probable.
4. The size of the molecules is much less than the average distance between them.
5. The molecule of a gas exert no force on each other except when they collide.
6. The collision between molecules and with walls are perfectly elastic.
7. The direction of molecular velocities are assumed to be distribute uniformly.
8. The molecules move with all speeds ranging from 0 to ∞.
9. The time of collision is much less than the time between collisions.

1.1.1 Pressure Exerted by a Gas

Suppose there are n molecules per cubic meter each of mass m, and its is assumed that n_i no. of molecule have velocity v_i.

Mathematically

$$\sum n_i = n \text{ and } v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2$$

where v_{ix} v_{iy} and v_{iz} are x, y, z component of velocity of gases.

From assume of kinetic theory of gases $v_{ix}^2 = v_{iy}^2 = v_{iz}^2 \quad = \frac{v_i^2}{3}$

suppose molecules are kept in the cubic container of parameter L.

A molecule moving in the x direction will have momentum mv_{ix} normal to face of the cube before collision

$$\Delta P_{ix} = mv_{ix} - (-mv_{ix}) = 2mv_{ix}$$

Force acting on the wall by molecule is $f_{ix} = \frac{n_i 2mv_{ix}}{\Delta t} = \frac{n_i 2mv_{ix}^2}{2L} == \frac{n_i mv_{ix}^2}{L}$

Pressure exert on the wall of container by molecule $P_{ix} = \frac{mn_i v_{ix}^2}{L^3}$

so that pressure in the *x* direction expected by all group

$$P_x = \sum P_{ix} = \frac{m}{L^3} \sum n_i v_{ix}^2$$

Average value of v^2 is given by

$$\left\langle v_x^2 \right\rangle = \frac{\sum_i n_i v_{ix}^2}{\sum n_i} = \frac{\sum_{i=1} n_i v_{ix}^2}{n}$$

For three dimensional system $\left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle = \left\langle v^2 \right\rangle$ and

for isotropic system $\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{\left\langle v^2 \right\rangle}{3}$

So P_x can be written as

$$P_x = \frac{m}{L^3} n \left\langle v_x^2 \right\rangle \ , \ P = P_x = \frac{1}{3} \frac{m}{L^3} n \left\langle v^2 \right\rangle \quad P = \frac{1}{3} \frac{mn \left\langle v^2 \right\rangle}{V}$$

$$PV = \frac{1}{3} mN \left\langle v^2 \right\rangle$$

where V is volume of the container and $\left\langle v^2 \right\rangle$ is average value of square of velocity.

1.2 Gas Law for Ideal Gases:

1.2.1 Boyle's Law

At constant temperature (T), the pressure (P) of a given mass a gas is inversely proportional to its volume (*V*)

$$P \propto \frac{1}{V}$$

1.2.2 Charle's Law

At constant pressure (P) the volume of a given mass of a gas is proportional to its temperature (T)

$$V \propto T$$

1.2.3 Avogadro's Law

At the same temperature and pressure, equal volume of all gases contain equal number of molecules (N).

$$N_1 = N_2$$

1.2.4 Graham's Law of Diffusion

When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion (r) at each gas is inversely proportional to square root at density of gas (ρ)

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Dalton's Law of Partial Pressure: The sum of pressure exerted (P) by each gas occupying the same volume as that of the mixture (P_1, P_2, P_3,….)

$$\mathrm{P} = P_1 + P_2 + P_3 + \ldots.$$

1.2.5 Ideal Gas Equation:

Consider a sample of an Ideal gas at pressure P, volume V and temperature T the gas follows the equation

$$PV = nRT$$

Where n is number of molecules and R is proportionality constant known as gas constant

$$R = 8.314 \text{ J/mol/K}$$

Boltzmann constant K is ratio between R to Avogadro number N_A $k_B = \frac{R}{N_A} = \frac{8.314}{6.03\times10^{23}}$

$$k_B = 1.3\times10^{-23}\, J/K$$

Example: Find the maximum attainable temperature of ideal gas in each process given by $p = p_0 - \alpha V^2$; where p_0, α and β are positive constants, and V is the volume of one mole of gas.

Solution: $$P = P_0 - \alpha V^2 \qquad \text{(i)}$$

Number of mole of gas = 1

We know $PV = nRT \quad \Rightarrow P = \frac{RT}{V}$ put in (i)

$$\frac{RT}{V} = P_0 - \alpha V^2 \quad \Rightarrow T = \frac{P_0 V}{R} - \frac{\alpha V^3}{R} \qquad \text{(ii)}$$

For T maximum, $\frac{dT}{dV} = 0 \Rightarrow \frac{P_0}{R} - \frac{3\alpha V^2}{R} = 0$

$V = \sqrt{\frac{P_0}{3\alpha}}$ put in (ii) one will get $T_{\max} = \frac{2}{3} P_0 \sqrt{\frac{P_0}{3\alpha}}$

Example: Two thermally insulated vessel 1 and 2 are filled with air. They are connected by a short tube with a value. The volume of vessels and the pressure and temperate of air in them are (V_1, P_1, T_1) and (V_2, P_2, T_2) respectively. Calculate the air temperate and pressure established after opening of value if air follow Ideal gas equation.

Solution: For vessel (1) $P_1V_1 = n_1RT_1 \qquad n_1 = \frac{P_1V_1}{RT_1}$

For vessel (2) $P_2V_2 = n_2RT_2 \qquad n_2 = \frac{P_2V_2}{RT_2}$

After opening the value let pressure volume and temperature is P, V, T

$$PV = nRT$$

$$V = V_1 + V_2$$

$$n = n_1 + n_2 = \frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2}$$

Hence system is isolated then

Energy of (1) + energy of (2) = energy of composite

$$\frac{3}{2} n_1 KT_1 + \frac{3}{2} n_2 KT_2 = \frac{3}{2}(n_1 + n_2)KT$$

$$n_1T_1 + n_2T_2 = (n_1 + n_2)/T.$$

$$T = \frac{n_1T_1 + n_2T_2}{n_1 + n_2}$$

$$= \frac{\frac{P_1V_1}{RT_1}T_1 + \frac{(P_2V_2)}{RT_2}T_2}{\frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2}} \Rightarrow T = T_1T_2\frac{(P_1V_1 + P_2V_2)}{P_1V_1T_2 + P_2V_2T_1}$$

$$PV = nRT \qquad P = \frac{nRT}{V} \qquad P = \frac{P_1V_1 + P_2V_2}{V_1 + V_2}$$

Example: A horizontal cylinder closed from one end is rotated with a constant angular velocity ω about a vertical axis passing through the open end of the cylinder. The outside air pressure is equal to p_0, the temperature to T, and the molar mass of air to M. Find the air pressure as a function of the distance r from the rotation axis. The molar mass is assumed to be independent of r.

Solution: Force equation of dr element.

$dF = (dm)r\omega^2$ if S is cross section area then

$$dP = \frac{dF}{S} = \left(\frac{dm}{S}\right)r\omega^2 \qquad dm = \left(\frac{S}{r\omega^2}\right)dP$$

Also we know

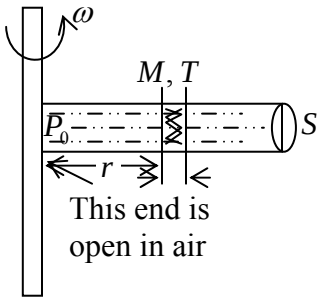
$$P(Sdr) = \left(\frac{dm}{M}\right)RT$$

$$PS(dr) = \frac{RT}{M}\left(\frac{S}{r\omega^2}\right)dP$$

$$M\omega^2\int_0^r rdr = RT\int_{P_0}^{P}\frac{dP}{P}$$

$$\frac{M\omega^2r^2}{2} = RT\ln\frac{P}{P_0}$$

$$P = P_0e^{\frac{M\omega^2r^2}{2RT}}$$



Example: Prove that $PA=\frac{1}{2}mN\langle v^2\rangle$ and $\langle E\rangle=\frac{2}{2}k_BT=k_BT$ in two dimension.

Solution: A molecule moving in the x direction will have momentum mv_{ix} normal to face of the cube before collision

$$\Delta P_{ix}=mv_{ix}-(-mv_{ix})=2mv_{ix}$$

Force acting on the wall by molecule is $f_{ix}=\frac{n_i 2mv_{ix}}{\Delta t}=\frac{n_i 2mv_{ix}^2}{2L}==\frac{n_i mv_{ix}^2}{L}$

Pressure exert on the wall of container by molecule $P_{ix}=\frac{mn_i v_{ix}^2}{L^3}$

So that pressure in the x direction expected by all group

$$P_x=\sum P_{ix}=\frac{m}{L^3}\sum n_i v_{ix}^2$$

Average value of v^2 is given by

$$\langle v_x^2\rangle=\frac{\sum_i n_i v_{ix}^2}{\sum n_i}=\frac{\sum_{i=1} n_i v_{ix}^2}{n}$$

For two dimensional system $\langle v_x^2\rangle+\langle v_y^2\rangle=\langle v^2\rangle$ and $\langle v_x^2\rangle=\langle v_y^2\rangle=\frac{\langle v^2\rangle}{2}$

So P_x can be written as

$$P_x=\frac{m}{L^2}n\langle v_x^2\rangle\ ,\ P=P_x=\frac{1}{2}\frac{m}{L^2}n\langle v^2\rangle \quad P=\frac{1}{2}\frac{mn\langle v^2\rangle}{A}$$

$$PA=\frac{1}{2}mN\langle v^2\rangle$$

1.3 Kinetic Interpretation of Temperature

According to assumption of Kinetic theory of gases, there is only translation motion of the molecule and there is not any potential acting between them, so

Average energy $\langle E \rangle$ of gases are equivalent to Average translation energy of a molecule

$$\langle E \rangle = \frac{1}{2} m \langle v^2 \rangle$$

Pressure at P as $P = \frac{1}{3} mn \langle v^2 \rangle = \frac{2}{3} n \left(\frac{1}{2} m \langle v^2 \rangle \right) = \frac{2}{3} n \langle E \rangle$

$$PV = \frac{2}{3} Vn \langle E \rangle \quad PV = \frac{2}{3} N \langle E \rangle \text{ where } n = \frac{N}{V} \text{ number density}$$

$$\langle E \rangle = \frac{3}{2} \frac{RT}{N_A} \text{ and } \langle E \rangle = \frac{3}{2} \left(\frac{R}{N_A} \right) T$$

$$\langle E \rangle = \frac{3}{2} K_B T \text{ where } k_B \text{ is Boltzman constant}$$

So average kinetic energy is given by

$$\langle E \rangle = \frac{3}{2} k_B T \text{ where T is absolute temperature.}$$

Example: It is possible to treat electromagnetic radiation in container whose wall is mirrors, as a gas of particle (photons) with a constant speed c and whose energy is related to their momentum p which is directed parallel to their velocity by $E = pc$ .Show that if container is full of radiation the equation of state is $PV = \frac{1}{3} E$

Solution: Pressure $P = \frac{1}{3} nm \langle v^2 \rangle = \frac{1}{3} n \langle mv \cdot v \rangle = \frac{1}{3} n \langle \vec{p} \cdot \vec{v} \rangle$

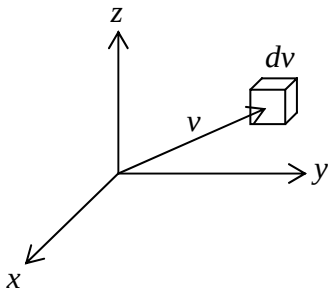
For Photon $v = c$ and velocity is parallel to momentum, so

$$P = \frac{1}{3} n \langle Pc \rangle \quad \Rightarrow \quad P = \frac{1}{3} \frac{N}{V} \langle pc \rangle$$

$$PV = \frac{1}{3} \langle Npc \rangle \quad \Rightarrow \quad PV = \frac{1}{3} E$$

1.4 Maxwell-Boltzmann Distribution Law:

Distribution of Molecular velocity in perfect gas.



Maxwell-Boltzmann distribution law is applicable for Ideal gas where molecules have no vibrational or rotational energies.

In the equilibrium state of the molecules have complete random motion and probability that a molecule has a given velocity component is independent of other two components.

In given figure dv is volume element in velocity space for a molecule at velocity $\vec{v} \equiv (v_x, v_y, v_z)$.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

We need to calculate number of molecules simultaneously having component in the range v_x to $v_x + dv_x, v_y$ to $v_y + dv_y$ and v_z to $v_z + dv_z$

It is assumptions in Maxwell-Boltzmann distribution law is that probability that molecule selected at random has velocities in a given range is a function purely at the magnitude of velocity and the width of the interval.

So fraction of molecule having velocity component in the range v_x to $v_x + dv_x, v_y$ to $v_y + dv_y$ and v_z to $v_z + dv_z$ is $f(v_x)dv_x$, $f(v_y)dv_y$ and $f(v_z)dv_z$ respectively.

$$\frac{dN}{N} = f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z$$

where dN is number of molecule having between velocity v to $v + dv$ and N is total number of molecules.

$$dN = N\, f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z$$

Number of molecule having velocity v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ is same as number of molecule having velocity v to $v + dv$.

So $$N\, f(v_x)f(v_y)f(v_z)dv_x\, dv_y\, dv_z = N\, F(v^2)dv_x dv_y dv_z$$

F is some function of v^2 (magnitude of velocity) and for fixed value of $\vec{v}$, $F(v^2)$ is constant.

So $dF(v^2)=0$ is equivalent to $d[f(v_x)f(v_y)f(v_z)]=0$

$$f'(v_x)dv_x f(v_y) f(v_z)+ f'(v_y)dv_y f(v_x) f(v_z)+ f'(v_z)dv_z\ f(v_x) f(v_y)=0$$

Dividing both side with $f(v_x)\ f(v_y)\ f(v_z)$

$$\frac{f'(v_x)}{f(v_x)}dv_x+\frac{f'(v_y)}{f(v_y)}dv_y+\frac{f'(v_z)}{f(v_z)}dv_z=0 \qquad \text{(i)}$$

$$v^2=\text{constant}\ \ v_x^2+v_y^2+v_z^2=v^2$$

$$v_x dv_x+v_y dv_y+v_z dv_z=0 \qquad \text{(ii)}$$

by method of Lagrange's method of undetermined multiplies multiply by 2β in equation (ii) and add in equation (i)

$$\left(\frac{f'(v_x)}{f(v_x)}+2\beta v_x\right)dv_x+\left(\frac{f'(v_y)}{f(v_y)}+2\beta v_y\right)dv_y+\left(\frac{f'(v_z)}{f(v_z)}+2\beta v_z\right)dv_z=0$$

hence v_x, v_y and v_z are independent

$$\frac{f'(v_x)}{f(v_x)}+2\beta v_x=0\Rightarrow\frac{f'(v_y)}{f(v_y)}+2\beta v_y=0\Rightarrow\frac{f'(v_z)}{f(v_z)}+2\beta v_z=0$$

$$f(v_x)=A_x e^{-\beta v_x^2} \qquad f(v_y)=A_y e^{-\beta v_y^2} \qquad f(v_z)=A_z e^{-\beta v_z^2}$$

$f(v_x), f(v_y), f(v_z)$ are probability density, so

$$\int_{-\infty}^{\infty} f(v_x)dv_x=1, \qquad \int_{-\infty}^{\infty} f(v_y)dv_y=1, \qquad \int_{-\infty}^{\infty} f(v_z)dv_z=1,$$

Use the integration

$$\int_0^{\infty} e^{-\beta v^2}v^n dv=\frac{1}{2\beta^{(\frac{n+1}{2})}}\left|\frac{n+1}{2}\right.$$

$$A_x\int_{-\infty}^{\infty} e^{-\beta v_x^2}dv_x=1\ \ =A_x\ \ 2\cdot\int_0^{\infty} e^{-\beta v_x^2}dv_x=1$$

$$A_x = \left(\frac{\beta}{\pi}\right)^{1/2} \text{ Similarly, } A_y = \left(\frac{\beta}{\pi}\right)^{1/2} A_z = \left(\frac{\beta}{\pi}\right)^{1/2}$$

$$f(v_x) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_x^2}, \quad f(v_y) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_y^2}, \quad f(v_z) = \left(\frac{\beta}{\pi}\right)^{1/2} e^{-\beta v_z^2}$$

$$\frac{dN}{N} = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta\left(v_x^2+v_y^2+v_z^2\right)} dv_x dv_y dv_z$$

where $-\infty < v_x < \infty$, $-\infty < v_y < \infty$, $-\infty < v_z < \infty$

1.4.1 The Distribution in Term of Magnitude

$v^2 = v_x^2 + v_y^2 + v_z^2$ which is equation of sphere and $dv_x dv_y dv_z$ can be replace by $4\pi v^2 dv$

$$f(v)dv = \frac{dN}{N} = \left(\frac{\beta}{\pi}\right)^{3/2} 4\pi e^{-\beta v^2} v^2 dv \qquad 0 < v < \infty$$

1.4.2 To Determine Value of β in Term of Temperature T.

Mean square velocity $\left(\langle v^2 \rangle\right)$ can be calculated by

$$\int_0^\infty v^2 f(v^2) dv$$

$$4\pi\left(\frac{\beta}{\pi}\right)^{3/2} \int_0^\infty v^4 e^{-\beta v^2} dv \quad \Rightarrow \quad 4\pi\left(\frac{\beta}{\pi}\right)^{3/2} \frac{1}{2\beta^{5/2}} \quad \boxed{5/2}$$

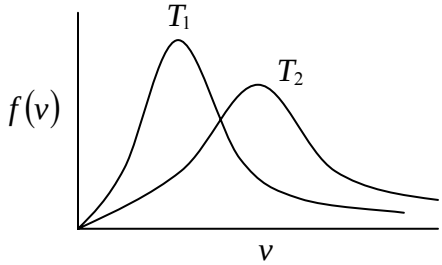
$$4\pi\left(\frac{\beta}{\pi}\right)^{3/2} \frac{1}{2\beta^{5/2}} \frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi} \quad \Rightarrow \quad \langle v^2 \rangle = \frac{3}{2}\cdot\frac{1}{\beta}$$

Now average energy of temperature T equivalent to

$$\frac{3}{2}k_B T = \frac{1}{2} m \langle v^2 \rangle$$

$$\frac{3}{2}k_B T = \frac{1}{2} m \quad \frac{3}{2}\frac{1}{\beta} \quad = \beta = \frac{m}{2k_B T}$$

So $$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{2k_B T}} dv_x dv_y dv_z$$



$T_1 < T_1$

$$f(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

1.4.2 Average Velocity

$$\langle v\rangle = \int_0^\infty v f(v)dv \qquad = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int e^{-\frac{mv^2}{2k_B T}} v^3 dv \;= \sqrt{\frac{8k_B T}{\pi m}}$$

1.4.3 Root Mean Square Velocity

$$\left[\langle v^2\rangle\right]^{1/2} = \left[\int_0^\infty v^2 f(v)dv\right]^{1/2}$$

$$= \left[4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\right]^{1/2}\left[\int_0^\infty e^{-\frac{mv^2}{2k_B T}} v^2 dv\right]^{1/2} = \sqrt{\frac{3k_B T}{m}}$$

1.4.4 Most Probable Velocity v_p :

$$\frac{df}{dv} = 0 \Rightarrow v_p = \sqrt{\frac{2k_B T}{m}}$$

Example: For Maxwellian gas find the $\langle v\rangle\times\left\langle\frac{1}{v}\right\rangle$

Solution: $\langle v\rangle=\sqrt{\frac{8k_BT}{\pi m}} \quad \Rightarrow\left\langle\frac{1}{v}\right\rangle=4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty\frac{1}{v}f(v)\;dv=\left(\frac{2m}{\pi k_BT}\right)^{1/2}$

$$\Rightarrow\langle v\rangle\times\left\langle\frac{1}{v}\right\rangle=\frac{4}{\pi}$$

Example: If v_x and v_y are x and y component of velocity then find the average value of $(av_x+bv_y)^2$

$$\left\langle(av_x+bv_y)^2\right\rangle=a^2\left\langle v_x^2\right\rangle+b^2\left\langle v_y^2\right\rangle+2ab\langle v_x\cdot v_y\rangle$$

$$=a^2\left\langle v_x^2\right\rangle+b^2\left\langle v_y^2\right\rangle+2ab\langle v_x\rangle\langle v_y\rangle$$

$$\langle v_x\rangle=\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}v_xe^{-\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{2k_BT}}dv_xdv_ydv_z=0$$

$$\left\langle v_x^2\right\rangle=\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}v_x^2e^{-\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{2k_BT}}dv_xdv_ydv_z=\frac{k_BT}{m}$$

Similarly, $\langle v_y\rangle=0 \qquad \left\langle v_y^2\right\rangle=\frac{k_BT}{m}$

$$\left\langle(av_x+bv_y)^2\right\rangle=a^2\left\langle v_x^2\right\rangle+b^2\left\langle v_y^2\right\rangle+2ab\langle v_x\rangle\langle v_y\rangle$$

$$=a^2\frac{k_BT}{m}+b^2\frac{k_BT}{m}+0=\frac{k_BT}{m}\left(a^2+b^2\right)$$

Example: Write down expression of energy distribution function for Maxwellian gas between E and $E+dE$. Hence find $\langle E\rangle$ down $\left\langle E^2\right\rangle$.

Solution: $E=\frac{1}{2}mv^2\;,dv=\frac{dE}{(2mE)^{1/2}}$

$$f(v)dv=4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}e^{-\frac{mv^2}{2k_BT}}v^2dv \quad \text{put value of } v \text{ and } dv$$

$$f(E)dE=\frac{2}{\sqrt{\pi}}\frac{1}{(k_BT)^{3/2}}e^{-\frac{E}{k_BT}}E^{1/2}dE \qquad 0<E<\infty$$

$$\langle E\rangle = \int_0^\infty Ef(E)dE \quad \langle E\rangle = \frac{3}{2}k_BT$$

$$\langle E^2\rangle = \int_0^\infty E^2 f(E)\ \ dE,$$

$$\langle E^2\rangle = \int_0^\infty E^2 \frac{2}{\sqrt{\pi}}\frac{1}{(k_BT)^{3/2}} e^{-\frac{E}{k_BT}} E^{1/2}dE = \frac{2}{\sqrt{\pi}}.(k_BT)^2.\frac{5}{2}.\frac{3}{2}\sqrt{\pi} = \frac{15}{2}.(k_BT)^2$$

Example: Write down expression of energy distribution function for Maxwellian gas between E and $E+dE$ in two dimensional system . Hence find $\langle E\rangle$.

$$E = \frac{1}{2}mv^2,\ dv = \frac{dE}{(2mE)^{1/2}}$$

$$f(v)dv = 2\pi\left(\frac{m}{2\pi k_BT}\right)^{2/2} e^{-\frac{mv^2}{2k_BT}} vdv \text{ put value of } v \text{ and } dv$$

$$f(E)dE = \frac{1}{(k_BT)} e^{-\frac{E}{K_BT}} dE \qquad 0 < E < \infty$$

$$\langle E\rangle = \int_0^\infty Ef(E)dE \Rightarrow \langle E\rangle = k_BT$$

Example: Using the Maxwell distribution function, calculate the mean velocity projection $\langle v_x\rangle$ the mean value of the modulus of the modulus of this projection $\langle |v_x|\rangle$ if the mass of each molecule is equal to m and the gas temperature is T.

Solution: We know Mean Velocity $= \langle v_x\rangle = \int_{-\infty}^{\infty}\frac{v_x dN}{N} = \frac{\int_{-\infty}^{\infty} v_x N\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{m}{2k_BT}v_x^2}dv_x}{N} = 0$

Mean speed $\langle |v_x|\rangle = \frac{\int_{-\infty}^{\infty}|v_x|N\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{m}{2k_BT}v_x^2}dv_x}{N}$

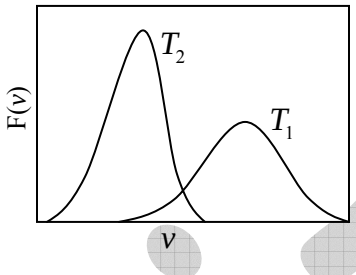
$$\langle |v_x|\rangle = \frac{2\int_0^{\infty} v_x N\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{m}{2k_BT}v_x^2}dv_x}{N} \Rightarrow \langle |v_x|\rangle = \sqrt{\frac{2k_BT}{\pi m}}$$

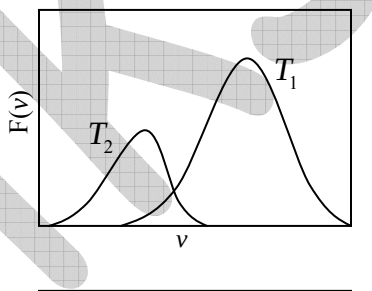
MCQ (Multiple Choice Questions)

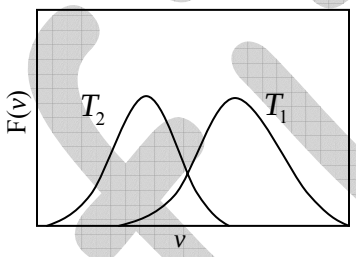
Q1. Consider a Maxwellian distribution of the velocity of the molecules of an ideal gas. Let v_{mp} and v_{rms} denote the most probable velocity and the root mean square velocity, respectively. The magnitude of the ratio $\frac{v_{rms}}{v_{mp}}$ is

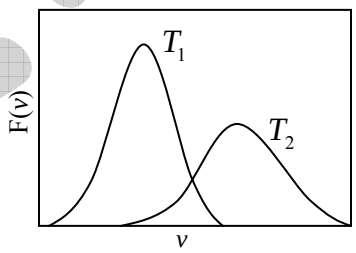
(a) $\sqrt{\frac{3}{2}}$ (b) 2/3 (c) $\sqrt{2/3}$ (d) 3 / 2

Q2. For temperature $T_1 > T_2$, the qualitative temperature dependence of the probability distribution $F(v)$ of the speed v of a molecule in three dimensions is correctly represented by the following figure

(a)


(b)


(c)


(d)


Q3. The speed v of the molecules of mass m of an ideal gas obeys Maxwell's velocity distribution law at an equilibrium temperature T . Let $(v_x, v_y v_z)$ denote the components of the velocity an k_B the Boltzmann constant. The average value of $(\alpha v_x - \beta v_y)^2$, where α and β are constants, is

(a) $(\alpha^2 - \beta^2) k_B T / m$ (b) $(\alpha^2 + \beta^2) k_B T / m$

(c) $(\alpha + \beta)^2 k_B T / m$ (d) $(\alpha - \beta)^2 k_B T / m$

Q4. The speed v of the molecules of mass m of an ideal gas obeys Maxwell's velocity distribution law at an equilibrium temperature T. Let $(v_x, v_y v_z)$ denote the components of the velocity and k_B the Boltzmann constant. The average value of $(\alpha v_x v_y)^2$, where α and β are constants, is

(a) 0

(b) $\alpha^2\left(\frac{k_B T}{m}\right)^2$

(c) $\alpha^2\left(\frac{k_B T}{2m}\right)^2$

(d) $\alpha^2\left(\frac{2k_B T}{m}\right)^2$

Q5. The statistical energy distribution underlying an ideal gas law gives the number of molecules with kinetic energies between E and $E + dE$ as $N(E)dE$. Which one of the following expressions can be used to obtain average kinetic energy over the collection of N molecules?

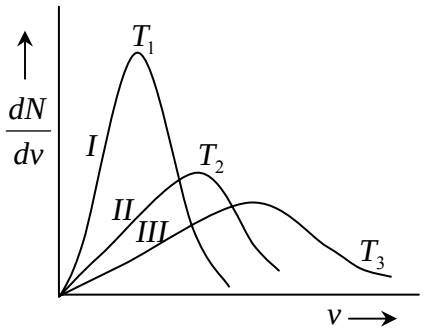
(a) $\frac{1}{N}\int_0^\infty EN(E)dE$

(b) $\frac{1}{N}\int_{-\infty}^{+\infty} N(E)dE$

(c) $\frac{1}{N}\int_0^\infty N(E)dE$

(d) $\frac{1}{N}\int_{-\infty}^{\infty} E\,dE$

Q6. The plots of Maxwell's distribution fraction $\left(\frac{dN}{dv}\right)$ *versus* speed (c) for a given sample of a gas at three different temperatures T_1, T_2 and T_3 respectively, are shown in the above diagram. If the areas on the c-axis under three curve I, II and III be denoted by A_{I}, A_{II} and A_{III} respectively, then which one of the following is correct?



(a) $A_{\text{I}} > A_{\text{II}} > A_{\text{III}}$

(b) $A_{\text{I}} = A_{\text{II}} = A_{\text{III}}$

(c) $A_{\text{I}} < A_{\text{II}} < A_{\text{III}}$

(d) $A_{\text{II}} < A_{\text{I}} < A_{\text{III}}$

Q7. Temperature of an ideal gas is increased such that the most probable velocity of molecules increase by a factor of 4. By what factor will the rms velocity increase?

(a) $\frac{\sqrt{3}}{2}$ (b)2 (c)4 (d)16

Q8. A gas at thermal equilibrium satisfying Maxwell's velocity distribution

Given $\bar{v}$ = average speed of the molecules

v_p = most probable speed

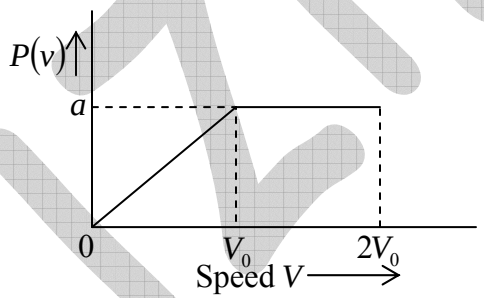
v_{rms} = root mean square speed

Select the correct sequence for $\bar{v}$, v_p, v_{rms} :

(a) $\bar{v} > v_{rms} > v_p$ (b) $v_{rms} > v_p > \bar{v}$

(c) $\bar{v} > v_p > v_{rms}$ (d) $v_{rms} > \bar{v} > v_p$

Q9. A hypothetical speed distribution for a sample of N gas particles is shown below. Here $P(v) = 0$ for $v > 2v_0$. How many particles have speeds between $1.2v_0$ and $1.9v_0$?



(a) $\frac{N}{5}$ (b) $\frac{7N}{15}$ (c) $\frac{2N}{21}$ (d) None of these

Q10. A parallel beam of nitrogen molecules moving with velocity v m/s impinges on a wall at an angle θ to its normal. The concentration of molecules in the beam n cm^3. The pressure exerted by the beam on the wall assuming the molecules to scatter in accordance with the perfectly elastic collision law is given by

(a) $2nmv^2 \cos\theta$ (b) $nmv^2 \cos\theta$

(c) $2nmv^2 \sin\theta$ (d) $nmv^2 \sin\theta$

Q11. If The mass of each molecule is equal to m then The temperature of a gas will the number of molecules, whose velocities fall within the given interval from v to $v+dv$ be the greatest

(a) $T=\frac{mv^2}{k_B}$ (b) $T=\frac{mv^2}{2k_B}$ (c) $T=\frac{mv^2}{3k_B}$ (d) $T=\frac{mv^2}{4k_B}$

Q12. Using the Maxwell distribution function, the mean value of the modulus of the modulus of this projection in x direction .e. $\langle |v_x| \rangle$ if the mass of each molecule is equal to m and the gas temperature T is given by

(a) 0 (b) $\sqrt{\frac{k_BT}{\pi m}}$ (c) $\sqrt{\frac{k_BT}{m}}$ (d) $\sqrt{\frac{2k_BT}{\pi m}}$

Q13. Making use of the Maxwell distribution function, if $\left\langle \frac{1}{v} \right\rangle$ the mean value of the reciprocal of the velocity of molecules in an ideal gas and $\langle v \rangle$ is the average velocity at a temperature T ,if the mass of each molecule is equal to m .then which one of the following is correct.

(a) $\left\langle \frac{1}{v} \right\rangle = \frac{1}{\langle v \rangle}$ (b) $\left\langle \frac{1}{v} \right\rangle = \frac{4}{\pi \langle v \rangle}$ (c) $\left\langle \frac{1}{v} \right\rangle = \frac{2}{\pi \langle v \rangle}$ (d) $\left\langle \frac{1}{v} \right\rangle = \frac{4\pi}{\langle v \rangle}$

Q14. If the root mean square velocity of hydrogen molecules exceeds their most probable velocity by Δv m/s then temperature is given by

(a) $T=\frac{m\Delta v^2}{k_B\left(\sqrt{3}-\sqrt{2}\right)^2}$ (b) $T=\frac{m\Delta v}{k_B\left(\sqrt{3}-\sqrt{2}\right)^2}$

(c) $T=\frac{m\Delta v}{\sqrt{k_B}\left(\sqrt{3}-\sqrt{2}\right)^2}$ (d) $T=\frac{m\Delta v}{k_B\left(\sqrt{3}-\sqrt{2}\right)}$

Q15. In the case of ideal gaseous in three dimensional the temperature at which the velocities of the molecules $v_1 m/s$ and $v_2 m/s$ are associated with equal values of the Maxwell distribution function $F(v)$

(a) $T = \dfrac{m\left(v_2^2 - v_1^2\right)}{4k_B \ln v_2 / v_1}$ (b) $T = \dfrac{m\left(v_2^2 + v_1^2\right)}{4k_B \ln v_2 / v_1}$

(c) $T = \dfrac{m\left(v_2^2 - v_1^2\right)}{4k_B \ln v_1 / v_2}$ (d) $T = \dfrac{m\left(v_2^2 + v_1^2\right)}{4k_B \ln v_1 / v_2}$

Q16. A gas consists of molecules of mass m and is at a temperature T in three dimension. Making use of the Maxwell velocity distribution function, the corresponding distribution of the molecules over the kinetic energies E is given by .

(a) $f(E)dE = \pi\left(\dfrac{1}{\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}} \sqrt{E}.dE$ (b) $f(E)dE = 2\pi\left(\dfrac{1}{\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}} \sqrt{E}.dE$

(c) $f(E)dE = \pi\left(\dfrac{1}{\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}} E.dE$ (d) $f(E)dE = 2\pi\left(\dfrac{1}{\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_B T}} E.dE$

Q17. A gas consists of molecules of mass m and is at a temperature T in two dimensions. Making use of the Maxwell velocity distribution function, the corresponding distribution of the molecules over the momentum p is given by

(a) $f(p) = \left(\dfrac{1}{2\pi m k_B T}\right) e^{-\frac{p^2}{2mk_B T}} pdp$ (b) $f(p) = \left(\dfrac{1}{mk_B T}\right) e^{-\frac{p^2}{2mk_B T}} pdp$

(c) $f(p) = \left(\dfrac{1}{2\pi m k_B T}\right) e^{-\frac{p^2}{2mk_B T}} dp$ (d) $f(p) = \left(\dfrac{1}{mk_B T}\right) e^{-\frac{p^2}{2mk_B T}} dp$

MSQ (Multiple Select Questions)

Q18. Consider the following statements related to kinetic theory of gases are correct:

(a) The molecules of a gas are all alike in size and shape and are hard, smooth, spherical particles.

(b) The size of the molecules is very small compared to the volume occupied by the gas.

(c) The molecules exert no appreciable force on one another except during a collision.

(d) The collisions of the molecules with the walls of the containing vessel are inelastic.

Q19. Consider the following statements. Which of the following is correct?

(a) The root mean square velocity of molecules of a gas having Maxwellian distribution of velocities, is higher than their most probable velocity, at any temperature.

(b) A very small number of molecules of a gas which posses very large velocities increase the root mean square velocity without affecting the most probable velocity

(c) Most probable velocity is lowest among the most probable velocity, average velocity and root mean square velocity.

(d) Mean square velocity is equal to square of mean velocity

Q20. Consider a collision between an oxygen molecule and a hydrogen molecule in a mixture of oxygen and hydrogen kept at room temperature. Which of the following are possible?

(a) The kinetic energies of both the molecules increase.

(b) The kinetic energies of both the molecules decrease.

(c) The kinetic energy of the oxygen molecule increases and that of the hydrogen molecule decreases.

(d) The kinetic energy of the hydrogen molecule increases and that of the oxygen molecule decreases.

Q21. Consider a mixture of oxygen and hydrogen kept at room temperature. As compared to a hydrogen molecule an oxygen molecule an oxygen molecule hits the wall

(a) with greater average speed (b) with smaller average speed

(c) with greater average kinetic energy (d) with smaller average kinetic energy

Q22. Which of the following quantities is zero on an average for the molecules of an ideal gas in equilibrium?

(a) any component of momentum (b) magnitude of momentum

(c) x component of velocity (d) speed

Q23. The average momentum of a molecule in a sample of an ideal gas depends on

(a) temperature (b) number of moles

(c) volume (d) mass of molecule

Q24. Which of the following quantities is the same for all ideal gases at the same temperature?

(a) The kinetic energy of 1 mole (b) The kinetic energy of $1g$

(c) The number of molecules in 1 mole (d) The number of molecules in 1 g

Q25. Which of the following is correct for ideal gas in two dimensional system

(a) The energy distribution is $f(E) \propto \exp -\left(\frac{E}{k_B T}\right) E^n$ the value of $n = 1$ for two dimensional function.

(b) The average kinetic energy is equal to $k_B T$

(c) The rms velocity of the gas is $\sqrt{\frac{3k_B T}{m}}$

(d) The most probable velocity of the gas is $\sqrt{\frac{k_B T}{m}}$

Q26. Keeping the number of moles, volume and temperature the same, which of the following are not the same for all ideal gases?

(a) rms speed of a molecule (b) density

(c) pressure (d) average magnitude of momentum

NAT (Numerical Answer Type)

Q27. At temperature …… ^0C the rms speed of gaseous hydrogen molecules equal to that of oxygen molecules at 47^0C .

Q28. Temperature of an ideal gas is increased such that the most probable velocity of molecules increase by a factor of 4. The rms velocity increase by the factor ……

Q29. If density of hydrogen gas is 0.1kg/m^3 and atmospheric pressure is $1.0\times10^5\ \text{N/m}^2$, then root mean square speed of hydrogen molecule is……m/sec

Q30. The temperature in Kelvin, at which the average speed of H_2 molecules will be same as that of N_2 molecules at 35^oC, will be……

Q31. Consider a Maxwellian distribution of the velocity of the molecules of an ideal gas three dimension. Let v_{mp} and v_{rms} denote the most probable velocity and the root mean square velocity, respectively. The magnitude of the ratio $\frac{v_{rms}}{v_{mp}}$ is……(Answer must be up to one decimal point)

Q32. Consider a Maxwellian distribution of the energy of the molecules of an ideal gas in three dimensions. Let E_{av} and E_{rms} denote the average energy and the root mean square energy, respectively. The magnitude of the ratio $\frac{E_{rms}}{E_{av}}$ is……(Answer must be up to one decimal point).

Q33. Consider a Maxwellian distribution of the velocity of the molecules of an ideal gas in two dimension. Let v_{av} and v_{rms} denote the average velocity and the root mean square velocity, respectively. The magnitude of the ratio $\frac{v_{rms}}{v_{av}}$ is……(Answer must be up to two decimal point)

Solutions

MCQ (Multiple Choice Questions)

Ans. 1: (a)

Solution: For Maxwellian distribution $v_{mp} = \sqrt{\frac{2k_BT}{m}}$, $v_{rms} = \sqrt{\frac{3k_BT}{m}} \Rightarrow \frac{v_{rms}}{v_{mp}} = \sqrt{\frac{3}{2}}$

Ans. 2: (a)

Solution: Area under the $f(v)$ curve is conserved and the mean velocity shift towards right for higher temperature.

Ans. 3: (b)

Solution: Ideal gas obeys Maxwell velocity distribution law at equilibrium temperature. Then average value of $\left(\alpha v_x - \beta v_y\right)^2$

Now $\left\langle \left(\alpha v_x - \beta_y\right)^2 \right\rangle = \left\langle \alpha^2 v_x^2 \right\rangle + \left\langle \beta^2 v_y^2 \right\rangle - 2\left\langle \alpha\beta v_x v_y \right\rangle$

$\langle v_x \rangle = 0, \langle v_y \rangle = 0$ and $\left\langle v_x^2 \right\rangle = \frac{k_BT}{m} = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle$

Then $\left\langle \left(\alpha v_x - \beta v_y\right)^2 \right\rangle = \alpha^2 \left\langle v_x^2 \right\rangle + \beta^2 \left\langle v_y^2 \right\rangle - 2\alpha\beta \langle v_x \rangle \langle v_y \rangle$

$\left\langle \left(\alpha v_x - \beta v_y\right)^2 \right\rangle = \alpha^2 \frac{k_BT}{m} + \beta^2 \frac{k_BT}{m} = \left(\alpha^2 + \beta^2\right)\frac{k_BT}{m}$

Ans. 4: (b)

Solution: Ideal gas obeys Maxwell velocity distribution law at equilibrium temperature. Then average value of $\left(\alpha v_x v_y\right)^2$

Now $\left\langle \left(\alpha v_x v_y\right)^2 \right\rangle = \left\langle \alpha^2 v_x^2 v_y^2 \right\rangle$

a $\left\langle v_x^2 \right\rangle = \frac{k_BT}{m} = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle$,Then $\left\langle \left(\alpha v_x v_y\right)^2 \right\rangle = \alpha^2 \left(\frac{k_BT}{m}\right)^2$

Ans. 5: (a)

Ans. 6: (b)

Solution: By Maxwell's distribution law the area, of graph between $\left(\frac{dN}{dv}\right)$ *versus* velocity v is same at all temperature. Hence, $A_I = A_{II} = A_{III}$

Ans. 7: (c)

Solution: $v_{rms} = \sqrt{\frac{3RT}{m}}$ (i)

Most probable velocity $v_p = \sqrt{\frac{2RT}{m}}$

From Equation (i) and (ii)

$\Rightarrow v_{rms}$ and v_p both proportional $\sqrt{T}$

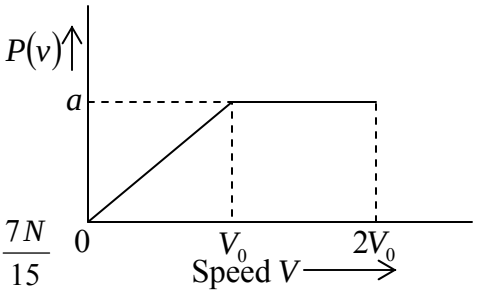
Ans. 8: (d)

Ans. 9: (b)

Solution: Since, total probability is one, hence area of the figure should be one

$$\Rightarrow \quad \frac{1}{2}av_0 + a(2v_0 - v_0) = 1$$

$$\Rightarrow \quad \frac{3}{2}av_0 = 1 \Rightarrow a = \frac{2}{3v_0}$$



now area between $v = 1.2v_0$ to $v = 1.9v_0 = \frac{2}{3v_0} \times (1.9v_0 - 1.2v_0) = \frac{7N}{15}$

Ans. 10: (a)

Solution: Momentum transfer in one collision $= 2mv\cos\theta$

Number of molecules collision per second $= n(vA)$

$$\left(\frac{dp}{dt}\right)_{mt} = nv(2mv\cos\theta)A$$

$$F = 2nmv^2\cos\theta$$

$$F/A = P = 2nmv^2\cos\theta$$

Ans. 11: (c)

Solution: $f(v)=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}} 4\pi v^2$

Here $v=$ constant but T is variable.

Then for $f(v)$ maximum. $\frac{df(v)}{dT}=0$

$$f(v)=\left(\frac{m}{2\pi k_B}\right)^{3/2}\left(T^{-3/2}e^{-\left(\frac{mv^2}{2k_B T}\right)}\right)4\pi v^2$$

$$\frac{df(v)}{dT}=0 \ ,\Rightarrow T^{-7/2}\frac{mv^2}{2k_B}=\frac{3}{2}T^{-5/2} \Rightarrow T=\frac{mv^2}{3k_B}$$

Ans. 12: (d)

Solution: $\langle|v_x|\rangle=\dfrac{\int_{-\infty}^{0}-v_x N\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m}{2k_B T}v_x^2}dv_x+\int_0^{\infty}v_x N\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{m}{2k_B T}v_x^2}dv_x}{N}=\langle|v_x|\rangle=\sqrt{\frac{2k_B T}{\pi m}}$

Ans. 13: (b)

Solution: $\left\langle\frac{1}{v}\right\rangle=\frac{\int_0^{\infty}\frac{1}{v}(dN)}{N}=\int_0^{\infty}\frac{1}{v}\left(\frac{dN}{N}\right)=\int_0^{\infty}\frac{1}{v}\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m}{2k_B T}v^2}4\pi v^2 dv$

$$\left\langle\frac{1}{v}\right\rangle=\sqrt{\frac{2m}{\pi k_B T}}=\frac{4}{\pi\langle v\rangle}$$

Ans. 14: (a)

Solution: $v_p=\sqrt{\frac{2k_B T}{m}}$ and $v_{rms}=\sqrt{\frac{3k_B T}{m}}$ $v_{rms}-v_p=\Delta v=\sqrt{\frac{3k_B T}{m}}-\sqrt{\frac{2k_B T}{m}}$

$$\Rightarrow\frac{\Delta v}{\left(\sqrt{3}-\sqrt{2}\right)}\sqrt{\frac{m}{k_B}}=\sqrt{T} \qquad \Rightarrow T=\frac{m\Delta v^2}{k_B\left(\sqrt{3}-\sqrt{2}\right)^2}$$

Ans. 15: (a)

Solution: $F(v)=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv/2k_BT}\,4\pi v^2$

Let temperature T at which for v_1 and v_2, $F(v)$ are same.

$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv_1^2/2k_BT}\,4\pi v_1^2=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv_2^2/2k_BT}\,4\pi v_2^2$$

Here range will be taken same for both

$$T=\frac{m\left(v_2^2-v_1^2\right)}{4k_B\ln\left(v_2/v_1\right)}$$

Ans. 16: (b)

Solution: $f(v)=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_BT}}\,4\pi v^2 dv$

$K.E.=E=\frac{1}{2}mv^2\Rightarrow v=\sqrt{\frac{2E}{m}}$ Differentiate: $dE=mvdv \quad\Rightarrow vdv=\frac{dE}{m}$

$$f(E)dE=\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_BT}}\,4\pi\sqrt{\frac{2E}{m}}.\frac{dE}{m}$$

$$f(E)dE=2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} e^{-\frac{E}{k_BT}}\sqrt{E}.dE$$

Ans. 17: (b)

Solution: In two dimensional $f(v)=\left(\frac{m}{2\pi k_B T}\right)e^{-\frac{mv^2}{2k_BT}}\,2\pi v dv$

$K.E.=\frac{1}{2}mv^2=\frac{p^2}{2m}$ $dp=mdv$ putting the value in $f(v)=\left(\frac{m}{2\pi k_B T}\right)e^{-\frac{mv^2}{2k_BT}}\,2\pi v dv$

$$f(p)=\left(\frac{m}{2\pi k_B T}\right)e^{-\frac{p^2}{2mk_BT}}\,2\pi\,\frac{p}{m}\frac{dp}{m} \quad\Rightarrow f(p)=\left(\frac{1}{mk_B T}\right)e^{-\frac{p^2}{2mk_BT}}\,pdp$$

MSQ (Multiple Select Questions)

Ans. 18: (b) and (d)

Solution: Kinetic theory of gases are based on the following assumptions:

(i) All gases are made up of tiny elastic particles known as molecules.

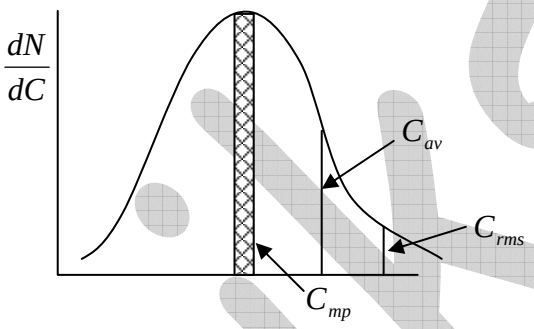
(ii) the volume of the molecule is negligible.

(iii) The collision between the molecules is elastic.

(iv) They exert no force on each other.

Ans. 19: (a), (b) and (c)

Solution:



Ans. 20: (c) and (d)

Solution: Momentum will transferred from one molecule to other as higher momentum will change to lower momentum and vice versa .

Ans. 21: (b)

Ans. 22: (a) and (c)

Ans. 23: (a) and (d)

Ans. 24: (a) and (c)

Ans. 25: (b) and (d)

Solution: For two dimension $f(E) \propto \exp-\left(\frac{E}{k_B T}\right)$ $\quad n = 0$

average energy is $\frac{\int_0^\infty E f(E) dE}{\int_0^\infty f(E) dE} = k_B T$

for two dimensional system $v_{rms} = \sqrt{\frac{2k_B T}{m}}$ $\quad v_{mp} = \sqrt{\frac{k_B T}{m}}$

Ans. 26: (a), (b) and (d)

Solution: Only pressure is not function of mass.

NAT (Numerical Answer Type)

Ans. 27: $-253^0 C$

Solution: $V_{rms} = \sqrt{\frac{3RT}{m}}$

$\Rightarrow \quad \sqrt{\frac{3RT_0}{m_0}} = \sqrt{\frac{3RT_H}{m_H}} = T_H = \frac{m_H}{m_0}(T_0)$

$m_H = 2amu, m_0 = 32\,amu$

and $T_0 = 47 + 273 = 320^0 C$

so, $T_H = \frac{2}{32}(320)$

$T_H = 20K \quad = T_H = (20 - 273)^0 C = -253^0 C$

Ans. 28: 4

Solution: $v_{rms} = \sqrt{\frac{3RT}{m}}$ and $v_p = \sqrt{\frac{2RT}{m}}$

$\Rightarrow v_{rms}$ and v_p are both proportional to $\sqrt{T}$

$\Rightarrow v_{rms}$ increases by 4 times

Ans. 29: 1710 m/s

Solution: By kinetic theory of gases the pressure exerted by the gas on the wall of container is given as

Pressure $P = \frac{1}{3} d \langle v^2 \rangle$

Here, $P = 1 \times 10^5$ N/m^2, $d = 0.1$kg/m^3.

So, by Eq. (i) $\langle v \rangle = \sqrt{\frac{3P}{d}}$

$$v_{rms} = \sqrt{\frac{3\times 1\times 10^5}{0.1}} = \sqrt{3\times 10^6}\,\text{m/s} = 1710\,\text{m/s}$$

Ans. 30: $T_H = 22K$

The average speed of a molecule of gas at constant temperature T is given as

$$v_{av} = \sqrt{\frac{8RT}{\pi M}} \Rightarrow \frac{v_H}{v_N} = \sqrt{\frac{T_H M_N}{M_H T_N}}$$

given, $v_H = v_N$

$$\Rightarrow \quad T_N M_H = T_H M_N$$

$$\Rightarrow \quad \frac{T_H}{T_N} = \frac{M_H}{M_N} = \frac{2}{28}$$

$$\Rightarrow \quad T_H = \frac{1}{14}\times T_N = \frac{1}{14}\times (273+35)$$

$$T_H = 22K$$

Ans. 31: 0.8

Solution: For Maxwellian distribution $v_{mp} = \sqrt{\frac{2k_B T}{m}}$, $v_{rms} = \sqrt{\frac{3k_B T}{m}} \Rightarrow \frac{v_{mp}}{v_{rms}} = \sqrt{\frac{2}{3}}$

Ans. 32: 1.8

Solution: $E_{av} = \frac{3k_B T}{2}$ $E_{rms} = \sqrt{\frac{15}{2}}.k_B T$

$$\frac{E_{rms}}{E_{av}} = \frac{\sqrt{\frac{15}{2}}}{\frac{3}{2}} = \frac{2.7}{1.5} = 1.8$$

Ans. 33: 2.25

Solution: $\langle v \rangle = v_{av} = \int_0^\infty v f(v) dv = \frac{m}{2\pi k_B T} \int_0^\infty v.e^{-\frac{mv^2}{2k_B T}} 2\pi v dv = \sqrt{\frac{\pi k_B T}{8m}}$

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = \frac{m}{2\pi k_B T} \int_0^\infty v^2 .e^{-\frac{mv^2}{2k_B T}} 2\pi v dv = \frac{2k_B T}{m}$$

$$v_{rms} = \sqrt{\frac{2k_B T}{m}}$$

In two dimension system $v_{rms} = \sqrt{\frac{2k_B T}{m}}$

$$\frac{v_{rms}}{v_{av}} = \frac{\sqrt{\frac{2}{1}}}{\sqrt{\frac{\pi}{8}}} = \frac{1.4}{.62} = 2.25$$

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Chapter - 2

Real Gases

2.1 Andrew's Experiment on Carbon Dioxide

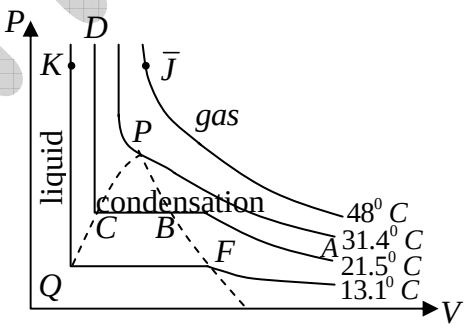
Andrew's experiment investigated the behaviour of CO_2 and analyse the Pressure (P) versus volume (V) at different temperature T.

The observations are following:

1. Above a temperature of about $(T = 48^0 C)$ the CO_2 resemble that of Ideal gas.
2. As temperature lowered, the isotherms exhibit distortion which gradually increases, which is indication from the ideal gas character.
3. At $31.4^0 C$ a Kink is observed which suggests the gas can be liquified under compression.
4. As temperature is lower further the kink spread into a horizontal line, i.e. compression produces liquification.

From A to B, CO_2 behave as a gas. At the point B the liquification of the gas just starts. The gas condenses at constant pressure from B to C so that liquid and vapour coexist. At C, the gas is completely in the liquid phase.

From C to D the slop is very steep since a liquid is almost incompressible.



Conclusion: The temperature at which it becomes possible to liquefy a gas under compression is known as critical temperature (T_C) [In Andrew experiment $(T_C) = 48^0 C$], corresponding pressure and volume is known as critical pressure (P_C) and critical volume (V_C).

A gas can be liquified only if it cooled upto or below its characteristic critical temperature.

There exist a continuity of liquid and gaseous states, i.e. they are two distinct stages at a continuous physical phenomenon.

2.2 van der Waals equation of state.

The van der Waals equation for real gases are given by

$\left(P+\frac{a}{V^2}\right)(V-b)=RT$ for 1 mole of gas and

$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$ for n mole of gas.

Assumption for real gas:

1. Gas molecules have finite size

2. There are weak interaction force, which depends only upon distance between them.

3. The molecular density is small and the number of collisions with the walls of the container are exactly the same point and finite size molecular.

2.3 Correction in Ideal Gas equation to achieve van der Waals gas equation of state.

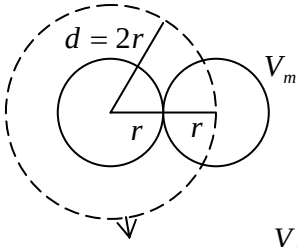
2.3.1 Correction for finite size: if V is volume available for one mole of gas (volume of container). If size of molecule take into account then $(V-b)$ is volume available for real gas which is less than V. b is popularly known as covolume which is dependent on the nature of gas.

Example: If V_m is molecular volume of real gas then prove that $b = 4NV_m$ if N is total number of molecule in container.

The volume available to first molecule = V

The volume available to second molecule = $V-V_s$

Where V_s volume of exclusion i.e. around any molecule, a spherical volume is $V_s=\left(\frac{4\pi d^3}{3}\right)$ will be denied to every other molecule.



Volume of exclusion $V_s=4\pi\frac{(2r)^3}{3}$

$V_s=8V_m$

Volume of exclusion $V_s=\frac{4\pi(2r)^3}{3}$

Similarly volume available to N^{th} molecule = $V - (N - 1)V_s$

Average volume available for each molecule

$$\langle V \rangle = \frac{1}{N}\sum_{i=1}^{N} V - (i-1)V_s = V - \frac{N(N-1)V_s}{2N} = V - \frac{N}{2}V_s = V - \frac{N}{2}8V_m = V - 4NV_m$$

$(V - b) = V - 4\,N\,V_m$ so $b = 4NV_m$

2.3.2 Correction for intermolecular attraction:

A molecule in the equally in all direction so that there is no resultant force on it.

But for outermost layer close to surface there will be net inward force. So whenever a molecule strikes the walls of container, the momentum exchange will be less than for Ideal gas.

There forces are cohesive in nature and proportional to number of molecule.

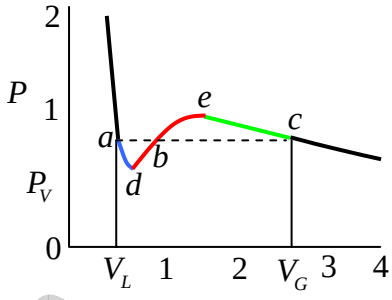
So for real gas change in pressure is $\frac{a}{V^2}$. So for real gas pressure will be $\left(P + \frac{a}{V^2}\right)$

So gas equation reduce to $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Then $P = \frac{RT}{V-b} - \frac{a}{V^2}$

2.3.3 Maxwell Equal Area

James Clerk Maxwell replaced the isotherm between a and c with a horizontal line positioned so that the areas of the two hatched regions are equal (means area of adb and bec are equal). The flat line portion of the isotherm now corresponds to liquid-vapor equilibrium. As shown in figure.



The portions $a-d$ and $c-e$ are interpreted as metastable states of **super-heated liquid** and **super-cooled vapor** respectively. The equal area rule can be expressed as:

$$P_V\left(V_G - V_L\right) = \int_{V_L}^{V_G} P dV$$

where P_V is the vapor pressure (flat portion of the curve), V_L is the volume of the pure liquid phase at point a on the diagram, and V_G is the volume of the pure gas phase at point c on the diagram. The sum of these two volumes will equal the total volume V .

Example One mole of a certain gas is contained in a vessel of volume V . At a temperature T_1 the gas pressure is p_1 atm and at a temperature T_2 the pressure is p_2 atm. Find the Van der Waals parameters for this gas.

Solution: it is given no of mole $n=1$

$$\left(P_1 + \frac{a}{V^2}\right)(V-b) = RT_1 \qquad \text{(i)}$$

$$\left(P_2 + \frac{a}{V^2}\right)(V-b) = RT_2 \qquad \text{(ii)}$$

from (i) and (ii)

$$a = \frac{V^2\left(T_1P_2 - T_2P_1\right)}{\left(T_2 - T_1\right)}$$

$$b = V - \frac{R\left(T_2 - T_1\right)}{\left(P_2 - P_1\right)}$$

Example: Under what pressure will carbon dioxide of molar mass M have the density ρ at the temperature T. If given gas is obeying for a Van der Waals gas.

Solution: Assume M is molar mass of the carbon dioxide and V is the volume so $\rho = \frac{M}{V}$

Van der wall equation (for one mole gas):

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(P + \frac{\rho^2 a}{M^2}\right)\left(\frac{M}{\rho} - b\right) = RT \quad \Rightarrow P = \frac{RT}{\left(\frac{M}{\rho} - b\right)} - \frac{\rho^2 a}{M^2} \Rightarrow P = \frac{\rho RT}{M - \rho b} - \frac{\rho^2 a}{M^2}$$

2.3.4 Critical Point

The van der Waals equation of state for a gas is given by

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where P, V and T represent the pressure, volume and temperature respectively, and a and b are constant parameters. At the critical point, where all the roots of the above cubic equation are degenerate means all roots are equal.

In another way mathematically For the critical isotherm is the point of inflection point

On basis of above definition one can find the critical volume V_c, critical pressure P_c and critical temperature T_c for van der waal gas.

For Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \text{(i)}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{for extremum point}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^2} = 0 \text{ at } V = V_c,\ T = T_c \qquad \text{(ii)}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad \text{for inflection point}$$

$$\frac{2RT}{(V-b)^3} - \frac{6a}{V^3} = 0 \qquad \text{at} V = V_c \ , \ T = T_c \qquad \text{(iii)}$$

solving (ii) and (iii)

$$V_c = 3b \qquad T_c = \frac{8a}{27Rb}$$

Put value of V_c and T_c one can get $P_c = \frac{a}{27b^2}$

$\frac{RT_c}{P_c v_c} = \frac{8}{3} = c_c$ which is popular known as **critical coefficient** for van der Waals gas.

2.3.5 van der Waals Equation of State and Virial Coefficient

According to virial theorem the equation of state is given by

$$pV = \alpha + \frac{\beta}{V} + \frac{\gamma}{V^2} + ... \qquad \text{(i)}$$

Where α, β and γ are first second and third virial coefficient .

For the Ideal gas $\alpha = RT$ and other coefficient are zero.

Virial coefficient for Van der Waals gas

To put van der Waals equation in virial form we first rewrite it as

$$pV = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

Using binomial theorem, we have

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + ...$$

Hence

$$pV = RT + \frac{RTb - a}{V} + \frac{RTb^2}{V^2} + ... \qquad \text{(ii)}$$

As will be noted, van der Waals equation has only three virial coefficients and a comparison with equation (i) yields

$$\alpha = RT,\ \beta = RTb - a \text{ and } \gamma = RTb^2$$

At the Boyle temperature, the second virial coefficient is zero. Hence,

$$RT_B b - a = 0$$

or $$T_B = \frac{a}{Rb}$$

From the preceding, section we recall that the critical temperature of a gas obeying van der Waals equation of state is

$$T_C = \frac{8a}{27Rb}$$

on comparing these expressions, we get

$$T_B = \frac{27}{8} T_C = 3.375\, T_C$$

that is, the Boyle temperature, on the basis of Van der Waals equation, is 3.375 times the critical temperature.

MCQ (Multiple Choice Questions)

Q1. A gas behaves as an ideal gas at:

(a) very low pressure and high temperature

(b) high pressure and low temperature

(c) high temperature and high pressure

(d) low pressure and low temperature

Q2. In the van der Waals equation, the terms $\left(\frac{a}{V^2}\right)$ and (b) are introduced to account for the:

(a) inter-molecular attraction and the total volume occupied by the gas

(b) molecular size and the size of the containing vessel

(c) inter-molecular attraction and the volume of the molecules

(d) inter-molecular attraction and the force exerted by the molecules on the walls of the container

Q3. 'Critical temperature' is defined as the:

(a) lowest temperature at which the gas can be liquefied at constant pressure

(b) lowest temperature at which the gas can be liquified by increase of pressure alone

(c) highest temperature at which the gas can beliquified by increase of pressure alone

(d) highest temperature at which the gas can be liquified at constant pressure

Q4. The work performed by one mole of a Van Der Waals gas during its isothermal expansion from the volume V_1 to V_2 at a temperature T is given by .

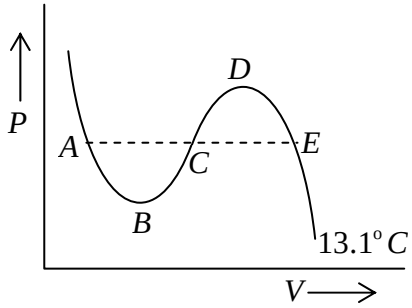
(a) $RT\ln\frac{V_2-b}{V_1-b}+a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$

(b) $RT\ln\frac{V_2-b}{V_1-b}+a\left(\frac{1}{V_1}-\frac{1}{V_2}\right)$

(c) $RT\ln\frac{V_1-b}{V_2-b}+a\left(\frac{1}{V_1}-\frac{1}{V_2}\right)$

(d) $RT\ln\frac{V_1-b}{V_2-b}+a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$

Q5.



Consider the above graph in respect of van der Waals equation of state. Which portion of the graph cannot be explained?

(a) AB (b) BC (c) DE (d) BCD

MSQ (Multiple Select Questions)

Q6. Which of the following are important in case of a van der Waals gas?

(a) Short range attraction (b) Long range repulsion

(c) Short range repulsion (d) Long range attraction

Q7. Which of the important results of Andrews' experiment are correct

(a) There exists a temperature called critical temperature, above which a gas cannot be liquefied, however great the applied pressure is.

(b) There exists a temperature called critical temperature, below which a gas cannot be liquefied, however great the applied pressure is.

(c) For van der Waal gases critical temperature is $\frac{a}{27Rb}$.

(d) Oxygen, nitrogen and hydrogen are permanent gases and they cannot be liquefied.

Q8. In the equation of state for real gases $\left(P+\frac{a}{V^2}\right)(V-b)=RT$

(a) The critical points are point of inflection.

(b) Critical volume is given by $V_c = 3b$

(c) Critical pressure is given by $P_c = \frac{a}{27b^2}$

(d) critical temperature is given by $T_c = \frac{8a}{27Rb}$

NAT (Numerical Answer Type Questions)

Q9. If the value of van der Waals constant b for a real gas is $32\,\text{cm}^3/\text{mol}$, then the approximate volume of one molecule of the gas i $\ldots\ldots\times 10^{-23}\ cm^3$ (Avogadro constant $= 6.02\times 10^{23}$) (Answer must be upto one decimal)

Q10. van der Waals equation predicts that the critical coefficient of a gas $\left(\frac{RT_c}{P_cV_c}\right)$ has the value……..(Answer must upto one decimal point)

Q11. If equation of state is given by $P=\frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ then critical volume $V_c=\ldots\ldots\ldots b$.

Q12. If equation of state is given by $P=\frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ then critical volume $T_c=\ldots\ldots\ldots\frac{a}{Rb}$.

Q13. If equation of state is given by $P=\frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ then critical coefficient $\frac{RT_c}{P_cV_c}=\ldots\ldots\ldots$

Solutions

MCQ (Multiple Choice Questions)

Ans. 1: (a)

Solution: The relation between PV and P is given as

$$PV = A + BP + CP^2 + DP^2 + \cdots \qquad \text{(i)}$$

$A, B, C \ldots$ are virial constant $A > B > C > D \ldots$. If P is very high then $PV \neq$ constant.

So, for ideal gas P should be small and T should be large.

Ans. 2: (a)

Solution: The ideal gas equation is $PV = RT$ whereas gas equation, for real gases is given by van der Waals which is $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ where, the factor b is due to volume occupied by the molecules itself and $\left(\frac{a}{V^2}\right)$ is due to molecular attractive force.

Ans. 3: (c)

Ans. 4: (a)

Solution: We know van der Waals gas equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{(i)}$$

$$\Delta W = \int dW = \int pdV$$

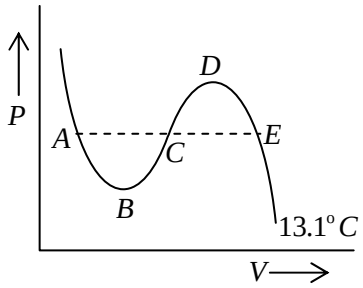
from (i): $$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

then $$W = \int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2}\right) dV$$

$$W = RT \ln \frac{V_2 - b}{V_1 - b} + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Ans. 5: (d)

Solution: The Van der Waals equation is given as



$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

where a,b are constant.

The graph drawn is shown as the curve $ABCDE$. This does not agree with the experimental isothermals for CO_2 as obtained by Andrews However the portion DE has been explained as due to super cooling of vapours and the portion AB due to super heating of the liquid. But the portion BCD cannot be explained because it shows decrease in volume with decrease in pressure.

MSQ (Multiple Select Questions)

Ans. 6: (c) and (d)

Solution: van der Waals equation $\left(P+\frac{a}{V^2}\right)(V-b)=RT$, where a,b are constant. In this case short range of repulsion and long range of attraction is important.

Ans. 7: (a) and (d)

Solution: From the result of Andrew's experiment we can define critical temperature as a temperature above which a gas cannot be liquefied however great the applied pressure is All gases are real gas so they can be liquefy

For van der Waals gases, critical temperature is given by $T_c=\frac{8a}{27Rb}$

Ans. 8: (a), (b), (c) and (d)

Solution: The van der Waals equation is given as

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$\left(\frac{\partial P}{\partial V}\right)_T=0$ and $\left(\frac{\mathrm{d}^2P}{dV^2}\right)_T=0$ (point of inflection) thus, we get $V_c=3b$

and $T_c=\frac{8a}{27Rb}\Rightarrow \quad P_c=\frac{a}{27b^2}$ Thus, $V_c=3b$

NAT (Numerical Answer Type Questions)

Ans. 9: 1.3

Solution: The van der Waals constant b is given as b = four times the actual volume of the molecules.

volume of one molecule $= \frac{b}{4N}$

volume of one molecule $= \frac{32}{4\times 6\times 10^{23}} = 1.3\times 10^{-23}\,\text{cm}^3$

Ans. 10: 2.6

Solution: For van der Waal Gases $T_c = \frac{8a}{27Rb}, V_c = 3b, P_c = \frac{a}{27b^2}$

$$\frac{RT_c}{P_cV_c} = \frac{8}{3}$$

Ans. 11: 2

Solution: $P = \frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ critical point are point of inflection so at critical points

$\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\mathrm{d}^2P}{dV^2}\right)_T = 0$ (point of inflection)

So $V_c = 2b$

Ans. 12: 0.25

Solution: $P = \frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ critical point are point of inflection so at critical points

$\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\mathrm{d}^2P}{dV^2}\right)_T = 0$ (point of inflection)

$V_c = 2b, T_c = \frac{a}{4bR}$

Ans. 13: 3.7

Solution: $P = \frac{RT}{V-b}\exp\left(-\frac{a}{RTV}\right)$ critical point are point of inflection so at critical points

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \text{ and} \left(\frac{\mathrm{d}^2 P}{dV^2}\right)_T = 0 \text{ (point of inflection)}$$

$$V_c = 2b, T_c = \frac{a}{4bR} \text{ and } P_c = \frac{a}{4e^2b^2}$$

fiziks

Chapter – 3

Basics of Thermodynamics and Laws of Thermodynamics

3.1 Mathematical Formulations of Thermodynamics.

$$y = y(x_1, x_2, ...x_n)$$

then differential *dy* is said to be exact and one can write

$$dy = \sum_i c_i dx_i$$

$$dy = c_1 dx_1 + c dx_2 + ... =$$

$$dy = \left(\frac{\partial y}{\partial x_1}\right) dx_1 + \left(\frac{\partial y}{\partial x_2}\right) dx_2 + ... = \sum_i \left(\frac{\partial y}{\partial x_i}\right) dx_i$$

and its corresponding c_i x_i are said to be conjugate to each other.

3.1.1 Some Important Formulas

1. $\frac{\partial^2 y}{\partial x_k \partial x_l} = \frac{\partial^2 y}{\partial x_l \partial x_k}$
2. $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z$
3. $\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x$
4. $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$
5. $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_Z \left(\frac{\partial w}{\partial y}\right)_z$
6. $dx = \left(\frac{\partial x}{\partial y}\right)_w dy + \left(\frac{\partial x}{\partial w}\right)_y dw$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$$

3.2 Fundamental Concept

3.2.1 System: A system can be any object, region of space etc, selected for study and set apart (mentally) from everything else. Which then become surrounding.

The system of interest in thermodynamics are finite and macroscopic rather than microscopic. The imaginary envelope which encloses a system and separated it from its surrounding is called the boundary of the system.

3.2.2 Isolated system It can not exchange either matter or energy with the surroundings.

If exchange of matter is allowed the system is said to be open; if only energy and not matter is closed (but not isolated).

3.2.3 Thermodynamical state

A thermodynamic state is a set of values of properties of a thermodynamic system that must be specified to reproduce the system.

Thermodynamic state is the macroscopic condition of a thermodynamic system as described by its particular thermodynamic parameter. Such as temperature (T) pressure (P) volume (V) density (ρ).

3.2.4 State function state function also called "State variable" thermodynamic variables describe the momentary condition of thermodynamic system

For a continuous process, such variable are exact different also fully determined by their initial and final thermodynamic states.

Example includes entropy, pressure, temperature, volume, etc.

3.2.5 Intensive and extensive properties

Intensive properties:-it is a physical property of a system that does not depend on the system size or the amount of material in system. It is scale invariant.

Example: Chemical potential, density, viscosity, resistivity, specific heat capacity, pressure, elasticity, magnetization, velocity, acceleration, temperatures, etc.

Solution: Extensive properties:- It is one that is additive for independent non-interacting subsystem. It is directly proportional to the amount of material in the system.

Example energy, Entropy, Gibbs energy, mass momentum, volume, change, weight,

Note: If f and g are arbitrary intensive variable then $fg, \frac{f}{g}, \frac{df}{dg}$ and $f+g$ will also intensive variable.

If F and G are also two arbitrary extensive variable then $F+G$ will an extensive variable but $\frac{F}{G}$ and $\frac{dF}{dG}$ will be intensive.

If F is extensive variable and f is intensive variable the f F and $\frac{F}{f}$ and $\frac{dF}{df}$ is extensive variable.

3.3 The Ideal Gas:

The Ideal gas law is the equation of hypothetical Ideal gas. It is derived from kinetic theory and satisfied Boyle's and Charles's law.

The state of an amount of ideal gas is determined by its pressure (P) volume (V) and temperature (T).

The Ideal gas equation of state for n mole is given by $PV = nRT$

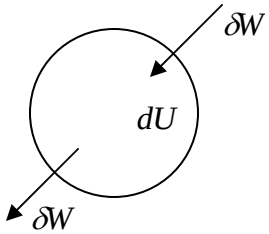
Where R is gas constant and given by 8.314 $J.K^{-1}$ $mole^{-1}$

3.4 Laws of Thermodynamics

3.4.1 Zeroth Law of Thermodynamics: If two systems 1 and 2 are separately in thermal equilibrium with third 3 they must be in thermal equilibrium with one another.

3.4.2 First Law of Thermodynamics: Energy is conserved when heat is taken into account.

Mathematically If δQ amount of heated to the system and if system will do δW amount of work then change in internal energy is dU given by



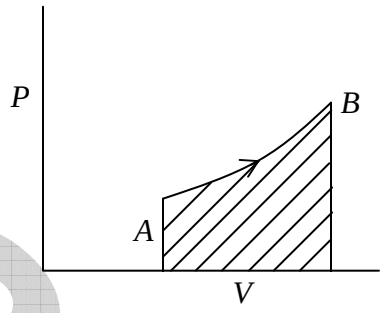
$$dU = \delta Q - \delta W$$

obviously heat exchange and work is dependent on path and internal energy is state function.

U is a mathematical abstraction that keeps account of the exchange of energy that be fall the system.

The term δQ means the amount of that amount of energy added to or remove by conduction of heat or by thermal radiation.

δW is amount of energy gained or lost as result of work.



3.4.3 Work Done during Different Process.

Work done when process is occur to between A to B

$$W = \int_A^B PdV$$

work done is area under the PV diagram.

If work is done by the system it has positive sign, and if work is done on the system it has negative sign.

3.4.4 Specific Heat:

Heat capacity of a body is numerically equal to quantity of heat required to raise its temperature by 1 unit.

$$C = \frac{\Delta\theta}{\Delta T}$$

The specific heat of a material is numerically equal to quantity of heat required to raise the temperature of unit mass of that materials through 1unit

$$C = \frac{d\theta}{mdT}$$

3.4.5 Heat Capacity of Ideal Gas: if f is degree of freedom of Ideal gas then from equipartition of energy total sum of energy is equivalent to sum of kinetic energy associated with each degree of freedom

3.4.6 Molar Heat Capacity: heat capacity defined as the energy required to raise the temperature of one mole of Ideal gas by one Kelvin at constant volume.

$U = \frac{f}{2} N_A KT$ where N_A is Avogadro number

$$\frac{dU}{dT} = \frac{f}{2} N_A K = \frac{fR}{2}$$

$C_V = \frac{Rf}{2}$, for Ideal gas

$$C_P = C_V + R = R\left(\frac{f}{2} + 1\right)$$

γ is defined as ratio of heat capacity at constant pressure to constant volume.

$$\gamma = \frac{C_p}{C_v} = \left(1 + \frac{2}{f}\right)$$

3.4.7 Coefficient of Volume Expansion (α) or expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

3.4.8 Isothermal Elasticity $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$ and **Isothermal compressibility** $\beta_T = \frac{1}{E_T}$

Example: Find the isothermal compressibility α of a Van der Waals gas as a function of volume V at temperature T.

Note: By definition, $\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.

Solution: We know bulk modulus of a gas is given by

Van der Wall equation: $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ (i)

If process is isothermal: $T = \text{constant}$

$$\left(dP + \frac{-a}{V^3} dV\right)(V - b) + \left(P + \frac{a}{V^2}\right)(dV) = 0$$

$$\left(\frac{dP}{dV}-\frac{a}{V^3}\right)(V-b)+\left(P+\frac{a}{V^2}\right)=0$$

$$\frac{dP}{dV}=-\frac{\left(P+a/V^2\right)}{(V-b)}+\frac{a}{V^3}=\frac{-\left(PV^3+aV\right)+a(V-b)}{V^3(V-b)}$$

$$\alpha=-\frac{1}{V}\left[\frac{V^3(V-b)}{\left(-PV^3+aV\right)+a(V-b)}\right]=\frac{V^2(V-b)}{\left[\left(PV^3-aV\right)+a(b-V)\right]} \qquad \text{(ii)}$$

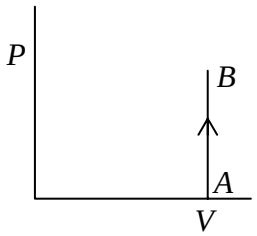
Put values of P from (i) in (ii)

$$\alpha=\frac{V^2(V-b)}{\left[RTV^3-2a(V-b)^2\right]}$$

3.5 Different Type of Thermodynamical Process and Use of First Law of Thermodynamics.

3.5.1 Isochoric Process: When volume remain constant during the process the process is said to be isochoric process.

$dW = PdV$ $\quad$ dV = 0 $\quad$ dW = 0



In an isochoric process work done during the process is zero.

From first law of thermodynamics.

$$dU=\delta Q-\delta W \qquad \delta W=0$$

$$dU=\delta Q=nC_V dT$$

In isochoric process change in interval is equal to heat exchange.

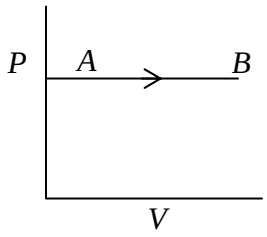
3.5.2 Isobaric Process: When pressure of the system remain constant during the process.

Work done during the process is given by

$$\int_A^B PdV = P(V_B-V_A)$$

$$= nR(T_B-T_A)$$

$$= nR\Delta T$$



where ΔT is change in temperature during the process.

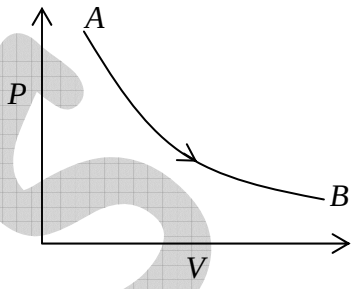
$$\delta Q=dU+\delta W=nC_V\Delta T+nR\Delta T=n\left(C_V+R\right)\Delta T$$

$\delta Q = nC_P \Delta T$ $\quad$ $C_V + R = C_P$ (for the ideal gas)

Heat exchange during the process for n mole of gas is equal to $nC_p\Delta T$ where C_p is specific heat capacity at constant process.

3.5.3 Isothermal Process: when temperature remains constant during the process then system is said isothermal process.

In isothermal process change in internal energy is zero because $\Delta T = 0$



$$\delta W = PdV = nRT\int_{V_A}^{V_B}\frac{dV}{V} \quad \Rightarrow \quad \delta W = nRT\ln\frac{V_B}{V_A}$$

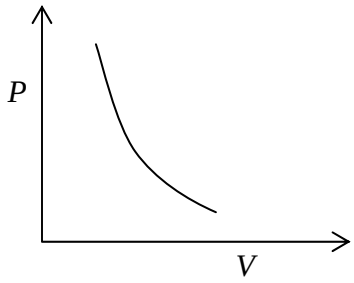
during the isothermal process heat exchange

$$\delta Q = \delta W \quad = nRT\ln\frac{V_B}{V_A}$$

3.5.4 Adiabatic Process: When there is not any heat exchange during the process then process is said to be adiabatic process.

Adiabatic process is defined by

$$PV^{\gamma} = \text{constant}$$



For Ideal gas PV = RT for one mole of gas.

So $TV^{\gamma-1} = \text{constant}$

$$P^{1-\gamma}T^{\gamma} = \text{constant}$$

where $\gamma = \frac{C_P}{C_V}$

work done during adiabatic process $\delta W = PdV$

$$PV^{\gamma} = k \quad dW = \frac{k}{V^{\gamma}}dV \quad = k\int_{V_A}^{V_B} V^{-\gamma}dV$$

$$k\frac{V^{-\gamma+1}}{-\gamma+1}\Big|_{V_A}^{V_B} = k\left(\frac{V_B^{1-\gamma} - V_A^{1-\gamma}}{1-\gamma}\right)$$

$$\frac{P_BV_B^{\gamma}V_B^{1-\gamma} - P_AV_A^{\gamma}V_A^{1-\gamma}}{1-\gamma} = \frac{P_BV_B - P_AV_A}{1-\gamma}$$

For n mole Ideal gas

$$W = \frac{nR(T_B - T_A)}{1-\gamma}$$

For Adiabatic process $\delta Q = dU + \delta W$

Hence $\delta Q = 0$ $\quad dU = -\delta W$

So in adiabatic process change in internal energy is equal to minus of work done i.e.

$$dU = \frac{nR(T_A - T_B)}{\gamma - 1}$$

Sign convention: Work done by the system is positive, work done on the system is negative, heat absorbed by system dQ is positive. Heat reject by the system is negative.

Example: n mole of certain ideal gas at temperature T_0 were cooled isochorically so that the gas pressure reduced n times. Then as a result at the isobaric process the gas expanded till its temperature get back to initial value. Find the total amount of heat absorbed by the gas in the process.

Solution: Let at state A, the pressure, volume, temperature is P_0, V_0, T_0, n is number of mole.

According to question:

$$\underset{(A)}{\frac{P_0V_0}{T_0}} \xrightarrow{\text{isochoric}} \underset{(B)}{\frac{P_0}{n}\frac{V_0}{T_B}} \xrightarrow{\text{isochoric}} \underset{(C)}{\frac{\frac{P_0}{n}V_c}{T_0}}$$

$$\frac{P_0V_0}{T_0} = \frac{P_0V_0}{nT_B} \qquad T_B = \frac{T_0}{n}$$

$$\frac{P_0}{n}\frac{V_0}{T_B} = \frac{P_0}{n}\frac{V_c}{T_0} = V_c = nV$$

In process A to B

$$dQ = nC_v\Delta T = nC_v\left(\frac{T_0}{n} - T_0\right)$$

In process B to C

$$dQ = nC_v\Delta T + PdV = nC_v\left(T_0 - \frac{T_0}{n}\right) + nR\left(T_0 - \frac{T_0}{n}\right)$$

Total heat absorbed by gas

$$dQ(A \to B) + dQ(B \to C)$$

$$= nC_v\left(\frac{T_0}{n} - T_0\right) + nC_v\left(T_0 - \frac{T_0}{n}\right) + nR\left(T_0 - \frac{T_0}{n}\right) = nRT_0\left(1 - \frac{1}{n}\right)$$

Example: A sample of an ideal gas is taken though the cyclic process *abca* as shown in figure. It absorbed 50 J of heat during part *ab*, no heat during bc and reject 70 J of heat during ca, 40 Jule of work is done on the gas during part *bc*.

(a) Find the internal energy of the gas at *b* and *c* if it is 1500 J at *a*.

(b) Calculate the work done by the gas during the part *ca*.

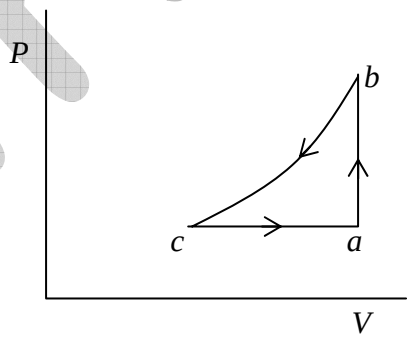
Solution: (a) during $a \to b$ V = constant

$$\Delta Q = dU = 50J$$

$U_a = 1500J$ so at $U_b = 1550J$

Work b $\to c$ = - 40 J

$U_b = 1550J$ $U_c = 1590$ (no heat at *bc*)



(b) during path c → a

$$\Delta U = 1500 - 1590 = -90J$$

$$\Delta Q = -70J$$

$$\Delta W = \Delta Q - \Delta U$$

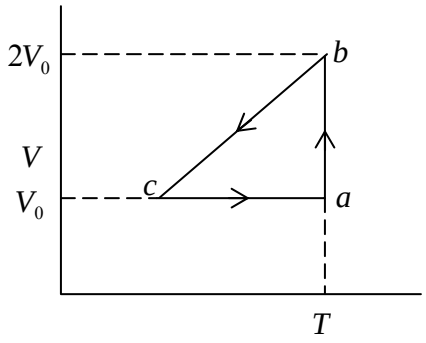
$$= -70 + 90 = 20J$$

Example: A sample of an Ideal gas has pressure P_0, volume V_0 and temperature T_0. It is isothermally expand to twice its original volume. It is then compressed at constant pressure to have the original volume V_0. Finally, the gas is heated at constant volume to get the original temperature.

(a) Show the process in VT diagram.

(b) Calculate the heat absorbed in the process.

Solution: (a)



(b) Hence the process is cyclic then change in internal energy in cycle is zero. So heat supplied in the cycle is equal to work done.

Work done during A → B is isothermal, so

$$W_{AB} = nRT_0 \ln \frac{2V_0}{V} \qquad = nRT_0 \ln 2$$

$b \to c$ isobaric, so work done is PdV.

$$P_a V_a = P_b V_b$$

$$P_0 V_{0a} = P_b 2V_0$$

$$P_b = \frac{P_0}{2}$$

$$W_{b\to c} = \frac{P_0}{2}(V_0 - 2V_0) = -\frac{P_0 V_0}{2}$$

$\mathrm{Wc} \to \mathrm{a}$ is isochoric $\mathrm{Wc} \to \mathrm{a} = 0$

Total work done is given by

$$nRT_0 \ln 2 + \left(-\frac{P_0 V_0}{2}\right)$$

$$= nRT_0\left(\ln 2 - \frac{1}{2}\right) \qquad \text{Ans.}$$

MCQ (Multiple Choice Questions)

Q1. The first law of thermodynamics is a statement of

(a) conservation of heat (b) conservation of work

(c) conservation of momentum (d) conservation of energy

Q2. If heat is supplied to an ideal gas in an isothermal process,

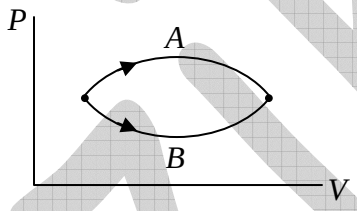
(a) the internal energy of the gas will increase

(b) the gas will do positive work

(c) the gas will do negative work

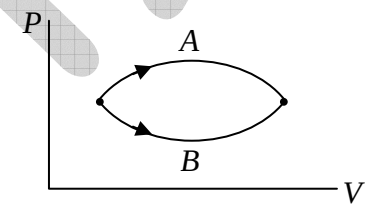
(d) the said process is not possible

Q3. Figure given below shows two processes A and B on a system. Let ΔQ_1 and ΔQ_2 be the heat given to the system in processes A and B respectively. Then



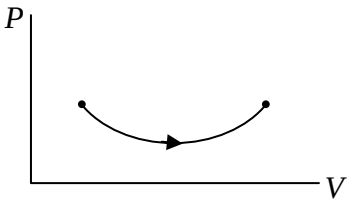
(a) $\Delta Q_1 > \Delta Q_2$ (b) $\Delta Q_1 = \Delta Q_2$ (c) $\Delta Q_1 < \Delta Q_2$ (d) $\Delta Q_1 \leq \Delta Q_2$

Q4. Refer to figure in Let ΔU_1 and ΔU_2 be the changes in internal energy of the system in the processes A and B. Then



(a) $\Delta U_1 > \Delta U_2$ (b) $\Delta U_1 = \Delta U_2$ (c) $\Delta U_1 < \Delta U_2$ (d) $\Delta U_1 \neq \Delta U_2$

Q5. Consider the process on a system shown in figure given below. During the process, the work done by the system



(a) continuously increases
(b) continuously decreases
(c) first increases then decreases
(d) first decreases then increases

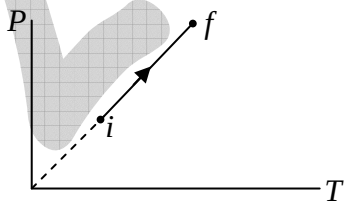
Q6. Consider the following two statements.

(A) If heat is added to a system, its temperature must increase.

(B) If positive work is done by a system in a thermodynamic process, its volume must increase.

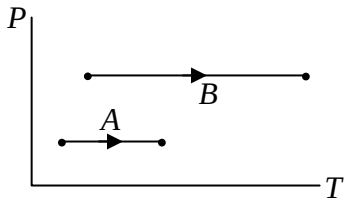
(a) Both A and B are correct
(b) A is correct but B is wrong
(c) B is correct but A is wrong
(d) Both A and B are wrong

Q7. An ideal gas goes from the state i to the state f as shown in figure below. The work done by the gas during the process



(a) is positive
(b) is negative
(c) is zero
(d) cannot be obtained from this information

Q8. Consider two processes on a system as shown in figure below.



The volumes in the initial states are the same in the two processes and the volumes in the final states are also the same. Let ΔW_1 and ΔW_2 be the work done by the system in the processes A and B respectively.

(a) $\Delta W_1 > \Delta W_2$ (b) $\Delta W_1 = \Delta W_2$ (c) $\Delta W_1 < \Delta W_2$

(d) Nothing can be said about the relation between ΔW_1 and ΔW_2.

Q9. A gas is contained in a metallic cylinder fitted with a piston. The piston is suddenly moved in to compress the gas and is maintained at this position. As time passes the pressure of the gas in the cylinder

(a) increases (b) decreases (c) remains constant

(d) increases or decreases depending on the nature of the gas.

Q10. The pressure and density of a gas $\left(\gamma = \frac{7}{5}\right)$ change adiabatically from (P_1, d_1) to (P_2, d_2).

If $\frac{d_2}{d_1} = 32$, then the value of $\left(\frac{P_2}{P_1}\right)$

(a) 32 (b) 128 (c) $\frac{1}{32}$ (d) $\frac{1}{128}$

Q11. The pressure P volume V and temperature T for a certain material are related by $P = \frac{\left(AT - BT^2\right)}{V}$ where A, B are constants. The work done by the materials if the temperature changes from T to $2T$ while the pressure remains constant?

(a) $AT - BT^2$ (b) $AT - 2BT^2$

(c) $AT - 3BT^2$ (d) $2AT - 3BT^2$

Q12. The specific heat (c) of a substance is found to vary with temperature (T) as $c = \alpha + \beta T^2$. Where T is Celsius temperature. At what temperature does the specific heat of the substance becomes equal to the mean specific heat of the substance in a temperature range between 0 and T_0 ?

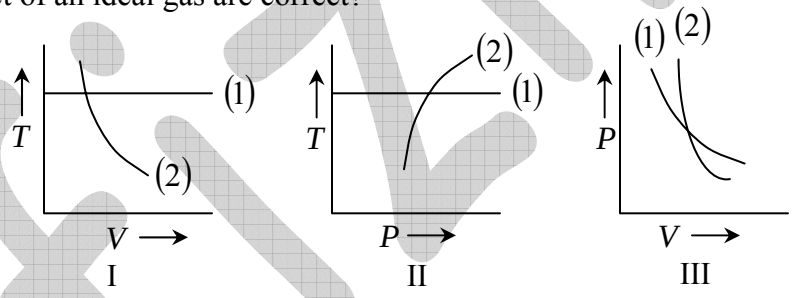
(a) $\frac{T_0}{\sqrt{2}}$ (b) $\frac{T_0}{2}$ (c) $\frac{T_0}{\sqrt{3}}$ (d) $\frac{T_0}{3}$

Q13. The equation of state of a gas is given as $P(V-b) = nRT$ where b is a constant, n is the number of moles and R is the universal gas constant. When 2 moles of this gas undergo reversible isothermal expansion from volume V to volume $2V$, what is the work done by the gas?

(a) $2RT\,In[(V-b)/(2V-b)]$ (b) $2RT\,In[(2V-b)/(V-b)]$

(c) $2RT\,In[(V-b)/(2V)]$ (d) $2RT\,In[(2V)/(V-b)]$

Q14. If (1) represents isothermal and (2) represents adiabatic, which of the graphs given above in respect of an ideal gas are correct?



(a) I and II (b) II and III (c) I and III (d) I, II and III

Q15. What is the minimum attainable pressure of an ideal gas in the process given by $T = a + bV^2$, where a, b are constants and V is the volume of one mole of ideal gas?

(a) $\sqrt{ab}$ (b) $R\sqrt{ab}$ (c) $2R\sqrt{ab}$ (d) $\sqrt{a/b}$

(R is the universal gas constant)

Q16. One mole of an ideal gas is takes from an initial state (P, V, T) to a final state $(2P, 2V, 4T)$ by two different paths as shown in the Fig. 1 and 2 given above. If the changes in internal energy between the final and the initial states of the gas along the paths I and II are denoted by ΔU_{I} and ΔU_{II} respectively, then:

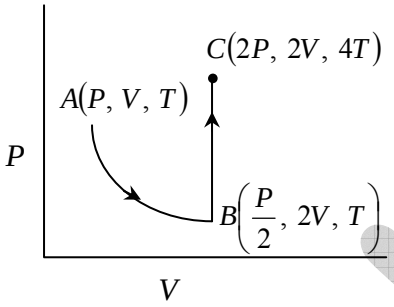


Fig. 1 (Path I)

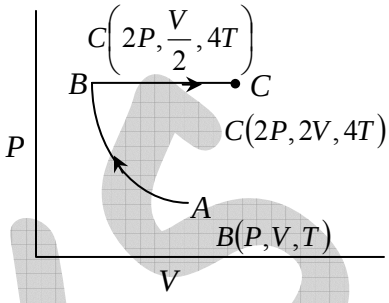
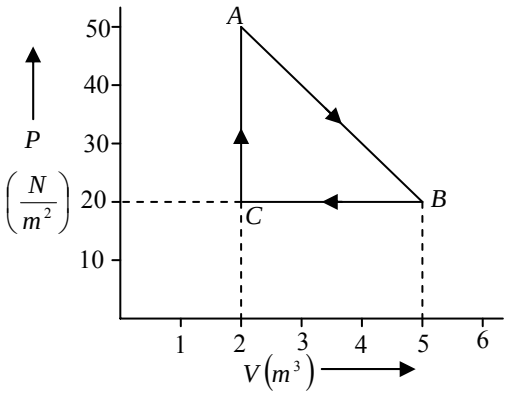


Fig. 2 (Path II)

(a) $\Delta U_{\text{I}} = \Delta U_{\text{II}}$ (b) $\Delta U_{\text{I}} > \Delta U_{\text{II}}$ (c) $\Delta U_{\text{I}} < \Delta U_{\text{II}}$ (d) $\Delta U_{\text{I}} = 0.66\,\Delta U_{\text{II}}$

Q17. A thermodynamic system is taken from an initial state A to another state B and back to state A via state C as shown by the path $A \to B \to C \to A$ in the $P-V$ diagram given then The work done by the system in going from the state A to the state B is:



(a) $35 \times 3.0\,J$ (b) $35 \times 3.5\,J$

(c) $50 \times 3.5\,J$ (d) $50 \times 5.0\,J$

Q18. A system absorbs $1.5 \times 10^3\,J$ of energy as heat and produces $500\,J$ of work. The change in the internal energy of the system will be:

(a) 1500 J (b) 100 J (c) - 1500 J (d) 1000 J

Q19. A given amount of heat cannot be completely converted into work. However it is possible to convert a given amount of work completely into heat. This apparently contradictory statement results from the:

(a) zeroth law of thermodynamics (b) first law of thermodynamics

(c) second law of thermodynamics (d) third law of thermodynamics

Q20. If the number of degrees of freedom of a molecule in a gas is n then the ratio of specific heats is given by:

(a) $1+\frac{1}{n}$ (b) $1+\frac{1}{2n}$

(c) $1+\frac{2}{n}$ (d) $\frac{2n}{2n-1}$

Q21. The ratio $\frac{\text{Slope of isothermal curve}}{\text{Slope of adiabatic curve}}$ is equal to:

(a) 1 (b) γ (c) $\frac{1}{\gamma}$ (d)2

Q22. One mole of a perfect gas expands adiabatically. As a result of this, its pressure, temperature and volume change from $P_1, T_1, V_1,$ to P_2, T_2 and V_2 respectively. if molar specific heat at constant volume is C_V, then the work done by the as is:

(a) $2.303 P_1 V_1 \log\left(\frac{V_2}{V_1}\right)$ (b) $RT_1 \log\left(\frac{V_2}{V_1}\right)$

(c) $\frac{P_1^2 V_1^2 - P_2^2 V_2^2}{R(T_2 - T_1)}$ (d) $C_V(T_1 - T_2)$

Q23. For a diatomic gas having 3 translational and 2 rotational degrees of freedom, the energy is given by:

(a) $\frac{5}{2}k_B T$ (b) $\frac{3}{2}k_B T$ (c) $\frac{1}{2}k_B T$ (d) $k_B T$

Q24. The maximum attainable temperature of ideal gas in each of the following processes $p = p_0 e^{-\beta V}$ is

(a) $T_{\max} = \frac{P_0}{e\beta R}$ (b) $T_{\max} = \frac{P_0}{2e\beta R}$ (c) $T_{\max} = \frac{2P_0}{e\beta R}$ (d) $T_{\max} = \frac{2P_0}{3e\beta R}$

Q25. A horizontal cylinder closed from one end is rotated with a constant angular velocity ω about a vertical axis passing through the open end of the cylinder. The outside air pressure is equal to p_0, the temperature to T, and the molar mass of air to M. Find the air pressure as a function of the distance r from the rotation axis. The molar mass is assumed to be independent of r.

(a) $P = P_0 e^{-\frac{M\omega^2 r^2}{2RT}}$ (b) $P = P_0 e^{\frac{M\omega^2 r^2}{2RT}}$ (c) $P = P_0 e^{-\frac{M\omega^2 r^2}{RT}}$ (d) $P = P_0 e^{\frac{M\omega^2 r^2}{RT}}$

Q26. A thermally insulated vessel containing a gas whose molar mass is equal to M and the ratio of specific heats $C_p / C_V = \gamma$ moves with a velocity v. If vessel is suddenly stopped then increment of temperature is given by

(a) $\Delta T = \frac{(\gamma - 1)}{R} Mv^2$ (b) $\Delta T = \frac{(\gamma - 1)}{2R} Mv^2$

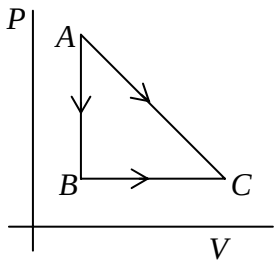
(c) $\Delta T = \frac{2(\gamma - 1)}{R} Mv^2$ (d) $\Delta T = \frac{(2\gamma - 1)}{R} Mv^2$

Q27. Gaseous hydrogen contained initially under standard conditions in a sealed vessel of volume V_0 was cooled by ΔT. The amount of heat will be lost by the gas if initial pressure is P_0 and temperature T_0

(a) $\Delta Q = \frac{P_0 V_0 \Delta T}{T_0 (\gamma - 1)}$ (b) $\Delta Q = \frac{\gamma P_0 V_0 \Delta T}{T_0 (\gamma - 1)}$

(c) $\Delta Q = \frac{P_0 V (\gamma - 1) \Delta T}{T_0}$ (d) $\Delta Q = \frac{P_0 V_0 (\gamma - 1) \Delta T}{\gamma T_0}$

Q28. A given quantity of gas is taken from the state $A \to C$ reversibly, by two paths, $A \to C$ directly and $A \to B \to C$ as shown in the figure. During the process $A \to C$ the work done by the gas is $100\,J$ and the heat absorbed is $150\,J$. If during the process $A \to B \to C$, the work done by the gas is $30\ J$, then which one of following is **correct?**



(a) heat absorbed in $A \to B \to C$ $20\,J$

(b) heat absorbed in $A \to B \to C$ $80\,J$

(c) heat reject in $A \to B \to C$ $20\,J$

(d) heat reject in $A \to B \to C$ $80\,J$

Q29. Let ΔQ be the heat exchange in a quasistatic reversible thermodynamic process. Then which of the following is correct?

(a) ΔQ is a perfect differential if the process is isothermal

(b) ΔQ is a perfect differential if the process is isochoric

(c) ΔQ is always a perfect differential

(d) ΔQ cannot be a perfect differential

Q30. Let ΔW be the work done in a quasistatic reversible thermodynamic process. Which of the following statements about ΔW is correct?

(a) ΔW is a perfect differential if the process is isothermal

(b) ΔW is a perfect differential if the process is adiabatic

(c) ΔW is always a perfect differential

(d) ΔW cannot be a perfect differential

MSQ (Multiple Select Questions)

Q31. The pressure p and volume V of an ideal gas both increase in a process.

(a) Such a process is not possible

(b) The work done by the system is positive

(c) The temperature of the system must increase.

(d) Heat supplied to the gas is equal to the change in internal energy.

Q32. In a process on a system, the initial pressure and volume are equal to the final pressure and volume.

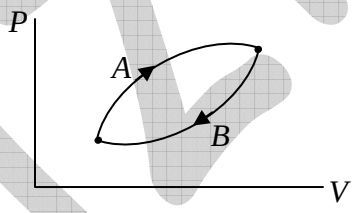
(a) The initial temperature must be equal to the final temperature.

(b) The initial internal energy must be equal to the final internal energy.

(c) The net heat given to the system in the process must be zero.

(d) The net work done by the system in the process must be zero.

Q33. Refer to figure below. Let ΔU_1 and ΔU_2 be the change in internal energy in processes A and B respectively, ΔQ be the net heat given to the system in process $A+B$ and ΔW be the net work done by the system in the process $A+B$.



(a) $\Delta U_1 + \Delta U_2 = 0$ (b) $\Delta U_1 - \Delta U_2 = 0$

(c) $\Delta Q - \Delta W = 0$ (d) $\Delta Q + \Delta W = 0$

Q34. The internal energy of an ideal gas decreases by the same amount as the work done by the system.

(a) The process must be adiabatic. (b) The process must be isothermal.

(c) The process must be isobaric. (d) The temperature must decrease.

Q35. Which of the following is correct statement statements?

(a) The value of $\frac{C_p}{(C_p + C_V)}$ for helium is $\frac{8}{3}$ for $\left(\gamma = \frac{5}{3}\right)$

(b) value of specific heat capacity at constant volume for helium is $\frac{3R}{2}$

(c) The value of $\frac{(C_p - C_V)}{(C_p + C_V)}$ for H_2 is $\frac{1}{6}$ for $\left(\gamma = \frac{7}{5}\right)$

(d) value of heat capacity at constant pressure is $\frac{7R}{2}$

Q36. The first law of thermodynamics, $\Delta U = \Delta Q - \Delta W$, indicates that when a system goes from its initial state to a final state which of following is **correct** statement

(a) ΔU is the same for every path

(b) ΔQ the same for every path in isochoric process

(c) ΔW is the same for every path in adiabatic process

(d) ΔW and ΔQ are the same for every path

Q37. Two thermally insulated vessels 1 and 2 are filled with air and connected by a short tube equipped with a valve. The volumes of the vessels, the pressures and temperatures of air in them are known $(V_1, p_1, T_1 \text{ and } V_2, p_2, T_2)$. The pressure established after the opening of the valve is given by

(a) $P = \frac{P_1V_1 + P_2V_2}{V_1 + V_2}$

(b) $P = \frac{P_1/V_1 + P_2/V_2}{\frac{1}{V_1} + \frac{1}{V_1}}$

(c) $P = \frac{T_1V_1 + T_2V_2}{V_1 + V_2}$

(d) $T = \frac{T_1T_2(P_2V_2 + P_1V_1)}{P_1V_1T_2 + P_2V_2T_1}$

Q38. Two moles of certain ideal gas at a temperature T_0 cooled isochorically so that the gas pressure reduced n times. Then, as a result of the isobaric process, the gas expanded till the temperature got back to the initial value.

(a) the work is given by RT_0

(b) the work is given by $2RT_0$

(c) the heat exchange is given by RT_0

(d) the heat exchange is given by $2RT_0$

NAT (Numerical Answer Type)

Q39. A diatomic gas at S T P is expanded to thirty-two times its volume under adiabatic conditions. the resulting temperature in …….. ^0K (answer must be in two decimal points)

Q40. The quantity of heat required to raise the temperature of one gram molecule through one degree for a mono atomic gas at constant volume is …….. R (where R is gas constant)

Q41. A gas expands adiabatically at constant pressure such that its temperature $T \propto \frac{1}{\sqrt{V}}$. The value of $\gamma\left(=\frac{C_p}{C_V}\right)$ of the gas is ……

Q42. One mole of diatomic gas $\left(C_V = \frac{5}{2}R\right)$ and one mole of a monatomic gas $\left(C_V = \frac{3}{2}R\right)$ are mixed. The value of γ for the mixture is, (where γ is the ratio of two specific heats of the gas……..

Q43. For a ideal gas having 3 translational and 2 rotational degrees of freedom at constant temperature T, the internal energy is …… k_BT

Q44. The minimum attainable pressure of ideal gas in the process $T = T_0 + \alpha V^2$ where T_0 and are positive constants, and V is the volume of one mole of gas is $\beta R\sqrt{\alpha T_0}$ the value of β is given by …….

Q45. The volume of one mole of an ideal gas with the adiabatic exponent γ is varied according to the law $V = a/T$, where a is a constant. Find the amount of heat obtained by the gas in this process if the gas temperature increased by ΔT.

Q46. Ten grams of ice at 0°C is added to a beaker containing 30 grams of water at 25°C. What is the final temperature of the system is ……. ^0C when it comes to thermal equilibrium? (The specific heat of water is 1 cal/gm/°C and latent heat of melting of ice is 80 cal/gm)

Solutions

MCQ (Multiple Choice Questions)

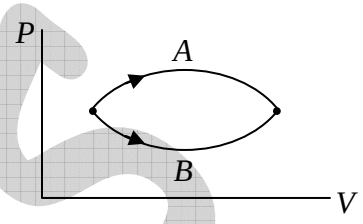
Ans. 1: (d)

Ans. 2: (b)

Solution: $dQ = dW$ sign dQ is positive so dW is positive the gas will do positive work .

Ans. 3: (a)

Solution: Change in internal energy in both the path is same and area under the path A is more than path B so work done in the path A is more than path B .From first law of thermodynamics $\Delta Q_1 > \Delta Q_2$



Ans. 4: (b)

Solution: Internal energy is point function

Ans. 5: (a)

Solution: work done is area under the curve so from the figure continuously increases

Ans. 6: (c)

Solution: From first law of thermodynamics sign of $dQ = dU + dW$ is not dependent only on change on temperature rather it can be compensated by sign of internal energy and work done .but work done is positive if volume expand .

Ans. 7: (c)

Solution: This is isochoric process so work done is zero

(d) Nothing can be said about the relation between ΔW_1 and ΔW_2 .

Ans. 8: (c)

Solution: The process is isobaric, so work done is $nRdT$ so change in temperature in B is more than A so $\Delta W_1 < \Delta W_2$

Ans. 9: (c)

Solution: After some time the system will be in mechanical equilibrium, so pressure will remain constant.

Ans. 10: (b)

Solution: If there is no exchange of heat between a system and its surrounding the process is known as adiabatic. The gas equation for adiabatic change is given as

$$PV^{\gamma} = \text{constant} \quad \text{since, volume} \propto \frac{1}{\text{density}} \ , \ P \propto (\text{density})^{\gamma}$$

$$\Rightarrow \qquad P_1 = kd_1^{\gamma} \qquad P_2 = kd_2^{\gamma} \qquad \frac{P_2}{P_1} = \left(\frac{d_2}{d_1}\right)^{\gamma}$$

$$\text{since,} \quad \frac{d_2}{d_1} = 32 \qquad \frac{p_2}{p_1} = (32)^{7/5} = \left(2^5\right)^{7/5} = 128$$

Ans. 11: (c)

Solution: Here,

$$P = \frac{AT - BT^2}{V}$$

where, A, B are constants.

The work done dW is given as

$$dW = PdV \qquad \text{(i)}$$

Now,

$$PV = AT - BT^2$$

$$\Rightarrow \qquad PdV = d\left(AT - BT^2\right)$$

$$\Rightarrow \qquad PdV = AdT - 2BT.dT \qquad \text{(ii)}$$

by equation (i) and (ii)

$$dW = AdT - 2BT.dT$$

$$\text{work done} = \int_T^{2T} (A - 2BT)dT \qquad = \left[AT - BT^2\right]_T^{2T} \qquad = A(2T - T) - B\left[(2T)^2 - T^2\right]$$

$$= AT - 3BT^2$$

Ans. 12: (c)

Solution: The amount of heat required to increase the temperature of unit mass is called specific heat.

$$Q = mc\Delta T$$

where $m =$ mass of substance

$\Delta T =$ increment in temperature

and $c = \alpha + \beta T^2$ (i)

The mean specific heat $\bar{c} = \frac{1}{T_0}\int_0^{T_0} c dT = \frac{1}{T_0}\int_0^{T_0}\left(\alpha + \beta T^2\right)dT = \frac{1}{T_0}\left[\alpha T_0 + \frac{\beta T_0^3}{3}\right]$

$$\bar{c} = \alpha + \frac{BT_0^2}{3}$$

By question $\bar{c} = c \quad \Rightarrow \alpha + \frac{BT_0^2}{3} = \alpha + BT^2 \Rightarrow \frac{BT_0^2}{3} = BT^2 \Rightarrow T = \frac{T_0}{\sqrt{3}}$

Ans. 13: (b)

Solution: $P(V-b) = nRT$

Work done $= dW = PdV$

$W = \int PdV$ where $P = \frac{nRT}{V-b}$ $W = \int_V^{2V}\frac{nRT}{V-b}dV$

$= nRT\int_V^{2V}\frac{dV}{V-b} = nRT\left[\log(2V-b) - \log(V-b)\right]$

Since, $n = 2$ $W = 2RT\log\left(\frac{2V-b}{(V-b)}\right)$

Ans. 14: (d)

Solution: Slope of adiabatic curve $= \gamma \times$ slope of isothermal curve. This is shown by every curve given in question. Hence, all curve represent the ideal gas.

Ans. 15: (c)

Solution: We have $T = a + bV^2 \quad \Rightarrow \frac{PV}{R} = a + bV^2$

$$\Rightarrow \qquad P = \frac{aR}{V} + \frac{V^2 Rb}{V} \qquad , P = \frac{aR}{V} + VbR$$

To find minimum pressure put $\frac{dP}{dV} = 0$

$$\Rightarrow \qquad \frac{d}{dV}\left[\frac{aR}{V} + VbR\right] = 0$$

$$\Rightarrow \qquad -\frac{aR}{V^2} + Rb = 0 \quad \Rightarrow V^2 = \frac{a}{b}$$

Again differential Eq. (i) twice, we get $\frac{d^2P}{dV^2}$ is +ve for V^2,

$$\Rightarrow \qquad P \text{ is minimum at } V^2.$$

By Eqs. (i) and (ii), we get

$$\Rightarrow \qquad P_{\min} = \frac{aR}{\sqrt{a/b}} + bR\sqrt{a/b} \qquad = 2R\sqrt{ab}$$

Ans. 16: (a)

Solution: The change in internal energy dU is independent of the path, i.e., if initial and final states of change are same then dU will be same.

Ans. 17: (a)

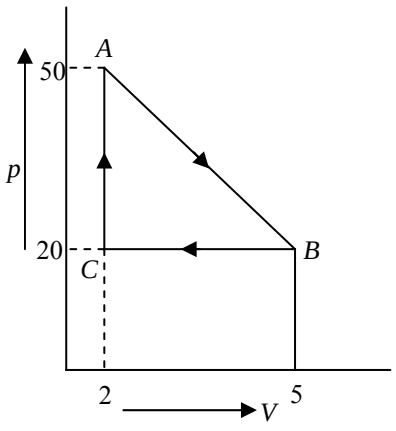
Solution: The work done is given as

$$= PdV$$

= area of the triangle + area of the rectangle

$$= \left[\frac{1}{2} \times (50 - 20) \times (5 - 2)\right] + (20 \times 3)$$

$$= \frac{1}{2} \times 30 \times 3 + 20 \times 3 \; = 105 \; J$$



Ans. 18: (d)

Solution: The first law of thermodynamics is given as

$$\delta Q = dU + \delta W$$

Here, $\delta Q = 1.5 \times 10^3 = 1500 J$

$\delta W = 500 J$

so, $dU = \delta Q - \delta W = 1000\ J$

Ans. 19: (b)

Ans. 20: (c)

Solution: We know that energy associated with each degree of freedom of one mole gas is given

$= \frac{1}{2} RT$

Hence if there is n degree of freedom, then $U = \frac{n}{2} RT$ where $R \rightarrow$ universal gas constant.

We know that specific heat at constant volume is given as

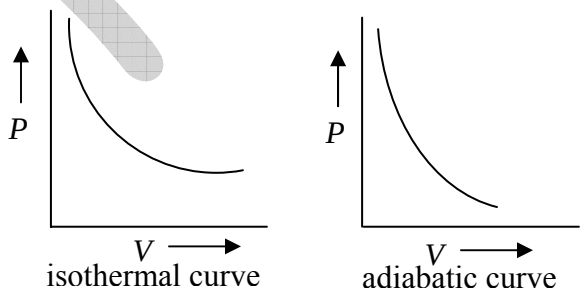
$$C_V = \frac{dU}{dT} \Rightarrow C_V = \frac{n}{2} R \qquad \text{(i)}$$

By Mayor's formula $C_P - C_V = R = R + \frac{n}{2} R \Rightarrow C_P = \left(1 + \frac{n}{2}\right) R$

$$\gamma = \frac{C_P}{C_v} \Rightarrow \gamma = 1 + \frac{2}{n}$$

Ans. 21: (c)

Solution:



isothermal curve adiabatic curve

The ideal gas equation is written as $PV = RT$

For isothermal T is constant differentiate above equation w.r.t. V we get

$\frac{d}{dV}(PV)=0 \Rightarrow \frac{dP}{dV}=-\left(\frac{P}{V}\right) \Rightarrow$ slope of isothermal curve $=-\frac{P}{V}$

In case adiabatic expansion gas equation is $PV^{\gamma}=$ constant .

differentiating this w.r.t. V we get $V^{\gamma}dP+\gamma PV^{\gamma-1}dV=0$

$\frac{dP}{dV}=-\gamma\left(\frac{P}{V}\right) \Rightarrow$ slope of adiabatic curve $=-\gamma\left(\frac{P}{V}\right)$ (ii)

dividing equation (ii), we get $\frac{\text{Slope of isothermal curve}}{\text{Slope of adiabatic curve}}=\frac{1}{\gamma}$

Ans. 22: (d)

Solution: Specific heat: The rate of change of internal energy w.r.t. temperature at constant volume is called specific heat at constant volume.

$$\Rightarrow \quad C_V=\left(\frac{dU}{dT}\right)_V \qquad \text{(i)}$$

by first law of thermodynamics $\Delta Q=dU+\Delta W$ (ii)

For adiabatic $\Delta Q=0$ so above equation (ii) becomes

$dU+\Delta W=0$

$\Rightarrow \quad C_V(dT)+\Delta W=0 \Rightarrow \quad C_V(T_2-T_1)+\Delta W=0 \quad \Rightarrow \Delta W=C_V(T_1-T_2)$

Ans. 23: (a)

Solution: The energy associated with each degree of freedom at temperature T is given as $E=\frac{1}{2}k_BT$, k_B is Boltzmann's constant

Here, total number of degrees of freedom= number of degree of rotational freedom + translational freedom $3+2=5$ thus, total energy $=5\times\frac{1}{2}k_BT$

Ans. 24: (a)

Solution: $P = P_0 e^{-\beta V} \Rightarrow \frac{RT}{V} = P_0 e^{-\beta V}$

$\Rightarrow T = \frac{P_0}{R} V e^{-\beta V}$ ….(i)

For maximum temperature, $\frac{dT}{dV} = 0 \Rightarrow \frac{P_0}{R}\left(e^{-\beta V} - \beta V e^{-\beta V}\right) = 0$

This gives $V = \frac{1}{\beta}$. Putting this value of V in equation (i), gives $T = \frac{P_0}{e\beta R}$

Ans. 25: (b)

Solution: Force equation of dr element.

$$dF = (dm)r\omega^2, \quad dP = \frac{dF}{A} = \left(\frac{dm}{A}\right)r\omega^2 \text{ and } dm = \left(\frac{A}{r\omega^2}\right)dP$$

where A is area of cross section

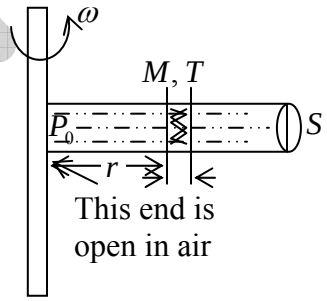
Also we know

$$P(Adr) = \left(\frac{dm}{M}\right)RT$$

$$PA(dr) = \frac{RT}{M}\left(\frac{A}{r\omega^2}\right)dP$$

$$M\omega^2 \int_0^r r dr = RT \int_{P_0}^{P} \frac{dP}{P}$$

$$\frac{M\omega^2 r^2}{2} = RT \ln \frac{P}{P_0} \Rightarrow P = P_0 e^{\frac{M\omega^2 r^2}{2RT}}$$



Ans. 26: (b)

Solution: Suppose number of moles of gas = n

Directional kinetic energy of gas = $\frac{1}{2}(nM)v^2$

When vessel sudden stop, then after long time this directional kinetic energy of gas is converted into random kinetic energy when thermodynamic equilibrium will be achieved and then $\frac{1}{2}(nM)v^2 = nC_V \Delta T \quad \Rightarrow \Delta T = \frac{(\gamma - 1)}{2R} Mv^2$

Ans. 27: (a)

Solution: Suppose initial temperature is T_1 and final is $(T_1 - \Delta T)$ then

$$U_i = \frac{P_1 V}{\gamma - 1}; \qquad U_f = \frac{P_2 V}{\gamma - 1}$$

$$\Delta U = \frac{V_0}{\gamma - 1}(P_2 - P_1)$$

$$P_1 V = nRT_1 \Rightarrow P_1 = \frac{nRT_1}{V} \text{ also } nR = \frac{P_1 V_0}{T_1}$$

$$P_2 = \frac{nRT_2}{V_0}$$

$$\Delta U = \frac{V_0}{\gamma - 1}\left(\frac{nRT_2}{V} - \frac{nRT_1}{V}\right) = \frac{nR}{\gamma - 1}(\Delta T)$$

$$\Delta U = \frac{P_1 V_0 \Delta T}{T_1(\gamma - 1)} \qquad \text{here } \begin{matrix} P_1 = P_0 \\ T_1 = T_o \end{matrix}$$

$$\Delta U = \frac{P_0 V_0 \Delta T}{T_0(\gamma - 1)}$$

ΔU = increase in potential energy

$$\Delta Q = \Delta U + \Delta W \qquad \text{since vessel is sealed then } \Delta W = 0$$

$$\Delta Q = \Delta U = \frac{P_0 V_0 \Delta T}{T_0(\gamma - 1)}$$

Ans. 28: (b)

Solution: During path AC $dU = \delta Q - \delta W = 150 - 100 = 50\ J$

Hence internal energy is point function dU will same in all path

In path ABC, $\delta Q = dU + \delta W = 50 + 30 = 80\ J$.

Ans. 29: (b)

Solution: Heat exchange is perfect differential in isochoric process.

$$\Delta Q = dU$$

Ans. 30: (b)

Solution: ΔW is a perfect differential if the process is adiabatic

$\Delta W = -d\mathrm{U}$

MSQ (Multiple Select Questions)

Ans. 31: (b) and (c)

Solution: If volume increase then workdone is positive and from $PV = nRT$ if volume and pressure increase then temperature will increase.

Ans. 32: (a) and (b)

Solution: from $PV = nRT$ if pressure and volume of initial point and final point is same then temperature is same ,so internal energy will also same

Ans. 33: (a) and (c)

Solution: $\Delta U_1 = \Delta U_2 = 0$ because internal energy is path independent so $\Delta Q - \Delta W = 0$

Ans. 34: (a) and (d)

Solution: $\delta Q = dU + \delta W$ and $dU = nC_V dT$, dU is negative so temperature decreases.

If $-dU = \delta W$ so $\delta Q = 0$

Ans. 35: (b), (c) and (d)

Solution: The ratio of C_p and C_V is known as coefficient of adiabatic expansion. Hence,

$$\gamma = \frac{C_p}{C_V}$$

(a) so, for helium $\gamma = \frac{5}{3} = \frac{1}{1+\frac{5}{3}}$, $\frac{C_p}{C_p + C_V} = \frac{3}{8}$

(b) $C_V = \frac{R}{\gamma - 1} = \frac{3R}{2}$ for $\left(\gamma = \frac{5}{3}\right)$

(c) for hydrogen $\gamma = \frac{7}{5} = \frac{C_p - C_V}{C_p + C_v}$

dividing by C_V the numerator and denominator, we get

$$\frac{C_p - C_V}{C_p + C_V} = \frac{C_p/C_V - 1}{C_p/C_V + 1} \qquad = \frac{\gamma - 1}{\gamma + 1} \qquad = \frac{\frac{7}{5} - 1}{\frac{7}{5} + 1} \qquad \Rightarrow \qquad \frac{C_p - C_V}{C_p + C_V} = \frac{1}{6}$$

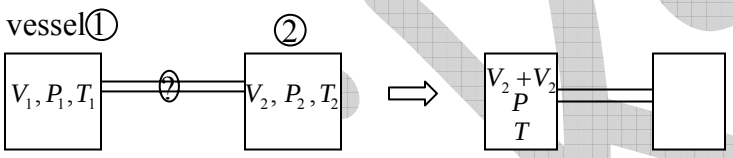
(d) $C_P = \dfrac{\gamma R}{\gamma - 1} = \dfrac{7R}{2}$

Ans. 36: (a), (b) and (c)

Solution: The internal energy ΔU is a state function. Hence, it does not depend on path whereas both Q and W depend on path. Thus, ΔQ is same for every path.

Ans. 37: (a) and (d)

Solution:



When value is opened and thermodynamics equilibrium is attained then, number of moles will be constant. Then

$$\frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_2} = \frac{P(V_1 + V_2)}{RT}$$

$$\frac{P_1V_1}{T_1} + \frac{P_2V_2}{T_2} = \frac{P(V_1 + V_2)}{T} \qquad \text{(i)}$$

Also we know, in whole system:

$$\Delta Q = 0 = \Delta U + \Delta W$$

$\Delta Q = 0$ because vessel is insulated. And also

$\Delta W = 0$ because gas does not work on atmosphere because vessel closed

then ΔU system = 0 then

$$n_1 C_V \Delta T_1 = n_2 C_V \Delta T_2 \qquad \Rightarrow \qquad n_1 \Delta T_1 = n_2 \Delta T_2$$

$$\frac{P_1V_1}{T_1}(T - T_1) + \frac{P_2V_2}{T_2}(T - T_2) = 0 \qquad \text{(ii)}$$

$$T = \frac{T_1T_2(P_2V_2 + P_1V_1)}{P_1V_1T_2 + P_2V_2T_1} \qquad \text{put in (i)} \quad P = \frac{P_1V_1 + P_2V_2}{V_1 + V_2}$$

Ans. 38: (a) and (c)

Solution:

$$\boxed{\begin{matrix} n=2 \\ T_0 \\ P_0 \end{matrix}} \quad V = \text{constant}, \quad P_f = \frac{P_0}{2}$$

Initial $(P_0;T_0;V) \xrightarrow{\text{isochoric}} \left(\frac{P_0}{2};T_1;V\right) \xrightarrow{\text{isobaric}} \left(\frac{P_0}{2};T_0;V\right)$

Here $PV = nRT$

$$P_0V = 2RT_0$$

$$V = \frac{2RT_0}{P_0}$$

Isochoric process:

$$\frac{P_1}{P_2} = \frac{T_1'}{T_2'}$$

$$\frac{P_0}{P_0/2} = \frac{T_0}{T_1} \quad \Rightarrow \quad T_1 = \frac{T_0}{2}$$

Isobaric process:

$$\frac{V_1'}{V_2'} = \frac{T_1'}{T_2'}$$

$$\frac{V}{V_2} = \frac{T_0/2}{T_0} \quad \Rightarrow \quad V_1 = 2V$$

In whole system: from initial to final position:

$$\Delta Q = \Delta U + \Delta W$$

here $\Delta U = 0$ final temperature is zero.

$$\Delta W = 0 + \frac{P_0}{2}[\Delta V] = \frac{P_0V}{2} = \frac{P_0}{2}\frac{2RT_0}{P_0}$$

$$\Delta W = RT_0 \text{ and } \Delta Q = RT_0$$

NAT (Numerical Answer Type)

Ans. 39: $68.25\,K$

Solution: For diatomic gas $\gamma = \frac{5}{2}$

$\therefore$ Adiabatic equation $TV^{\gamma-1} =$ constant

$$\Rightarrow \qquad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

here, $V_1 = V, V_2 = 32V, T_1 = 273K$

$$T_2 = \frac{273}{(32)^{\gamma-1}} \qquad \Rightarrow \qquad T_2 = \frac{273}{(32)^{\frac{5}{2}-1}} = \frac{273}{(32)^{\frac{3}{2}}} \qquad = 68.25\,K$$

Ans. 40: (a)

Solution: The quantity of heat required to increase the temperature at constant volume through $0°C$ for per degree of freedom

$$(Q)_V = nC_V dT$$

$$C_V = \frac{1}{2}R \qquad n = 1, \quad dT = 1$$

So, $$(Q)_V = 1 \times \left(\frac{1}{2}R\right) \times 1 = 0.5R$$

Ans. 41: 1.5

Solution: We know that for adiabatic expansion $TV^{\gamma-1} =$ constant

Given that $T \propto \frac{1}{\sqrt{V}} \Rightarrow TV^{1/2} = constant$

by equation (i) and (ii),

$$\gamma - 1 = \frac{1}{2} \Rightarrow \gamma = 1 + \frac{1}{2}, \ \gamma = \frac{3}{2} = 1.50$$

Ans. 42: 1.5

Solution: $c_V = \dfrac{n_1 c_{V_1} + n_2 c_{V_2}}{n_1 + n_2}$ and $c_P = \dfrac{n_1 c_{P_1} + n_2 c_{P_2}}{n_1 + n_2}$ $\gamma = \dfrac{c_p}{c_V}$

$n_1 = 1, c_{V_1} = \dfrac{5R}{2}, c_{P_1} = \dfrac{7R}{2}$ $n_1 = 1, c_{V_1} = \dfrac{3R}{2}, c_{P_1} = \dfrac{5R}{2}$

Ans. 43: 2.5

Solution: The energy associated with each degree of freedom at temperature T is given as $E = \dfrac{1}{2}k_B T$ is k_B Boltzmann's constant

Here, total number of degrees of freedom= number of degree of rotational freedom + translational freedom $3 + 2 = 5$thus, total energy $= 5 \times \dfrac{1}{2}k_B T$

Ans. 44: 2

Solution: $T = T_0 + \alpha V^2$

We know $PV = nRT = RT$

If V is increasing, T will increase and hence P will increase. Hence calculation of $P_{\min}$:

$T = \dfrac{PV}{R}$ put in (i)

$\dfrac{PV}{R} = T_0 + \alpha V^2$, $P = R\left[T_0 V^{-1} + \alpha V\right]$

$\dfrac{dP}{dV} = 0$, $R\left[-T_0 V^{-2} + \alpha\right] = 0 \Rightarrow V = \sqrt{\dfrac{T_0}{\alpha}}$ put in (ii)

Put the value of $V = \sqrt{\dfrac{T_0}{\alpha}}$ in $P = R\left[T_0 V^{-1} + \alpha V\right]$

$P_{\min} = 2R\sqrt{\alpha T_0}$

Ans. 45: 2

Solution: $V = \frac{a}{T}$ number of mole $n = 1$

$\Rightarrow \quad T = \frac{a}{V}$

we know $\delta Q = dU + \delta W$

$\Delta U = \int dU = C_V \Delta T = \frac{R}{\gamma - 1}\Delta T$ (i)

$\delta W = PdV \quad \Rightarrow \quad \Delta W = \int PdV$ (ii)

$PV = nRT = RT$

$P = \frac{RT}{V} = \frac{aR}{V^2}$ put in (ii)

$\Delta W = \int_{V_1}^{V_2} \frac{aR}{V^2} dV = -aR\frac{1}{V}\Big|_{V_1}^{V_2} = aR\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$

$\Delta W = \left[\frac{a}{V_1} - \frac{a}{V_2}\right]R = -R[\Delta T]$

$\Delta Q = \Delta U + \Delta W$

$= \frac{R\Delta T}{\gamma - 1} - R\Delta T = R\Delta T\left(\frac{1 - \gamma + 1}{\gamma - 1}\right)$

$\Delta Q = \frac{R\Delta T(2 - \gamma)}{\gamma - 1}$

Ans. 46: 0

Solution: The amount of heat required to melt the ice of mass 10gm at 0^0C is

$Q = m \times L = 10 \times 80 = 800Cal$. Where L is the latent heat of melting of ice and m is the mass of the ice. The amount of heat available in water of mass 30gm at 25^0C is

$Q = m \times C_v \times T = 30 \times 1 \times 25 = 750Cal$

Since the heat available is less than the heat required to melt the ice therefore ice will not melt as a result the temperature of the system will be at 0^0C only

Chapter – 4

Second Law of Thermodynamics and Entropy

4.1 Second Law of Thermodynamics

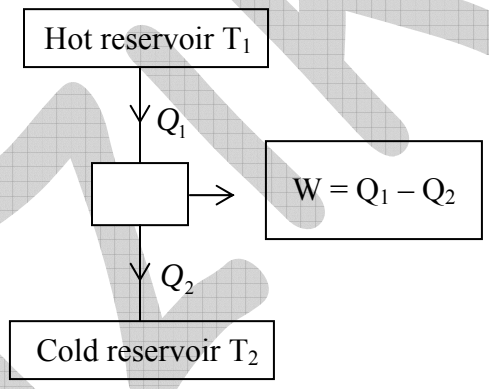
Statement: It is impossible to transfer total heat into work in a cyclic process in the absence of other effect (by Lord Kelvin).

In another way it is also stated that it is impossible for heat to be transferred by a cyclic process from a body to one warmer than itself without producing other changes at same time.

4.2 Heat Engines

A machine that can convert heat into work is said to be heat engine.

It is a system that performs the conservation of heat or thermal energy to mechanical work.



Schematic of operation at heat engine

4.2.1 Heat Reservoir

It is an effectively infinite pool of thermal energy of a given, constant temperature. Ideal its heat capacity is large enough that when it is in thermal contact with another system, its temperature remains constant.

All heat engines have mainly three essential components.

1. A source: This is a hot region which is a part of the surrounding from which energy flows by heat transfer. Popularly it is known as hot reservoir. Example is a nuclear reactor, furnace.

2. The working agent: This under goes change at state as part of a continuous cycle e.g. steam-water.
3. A sink: This is a respectively cold region which is part or the surrounding into which heat is rejected by heat transfer e.g. cooler.

4.2.2 Efficiency of Heat Engine (η):

$$\eta = \frac{\text{work done by the system}}{\text{heat given into the system}}$$

Hence the process is cyclic $dU = 0$.

$$dQ = dW$$

Heat given to system is Q_1 and heat rejected by system is Q_2.

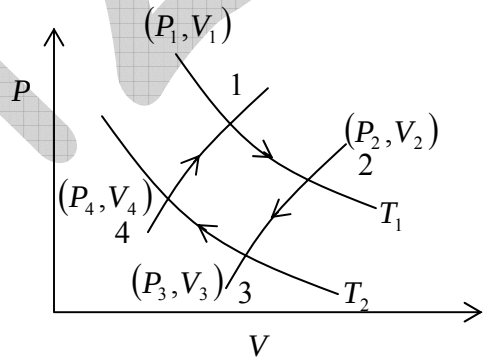
$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

4.2.3 Carnot Cycle: It is theoretical thermodynamics cycle proposed by Nicolas, Leonard Sadi Carnot.

It can be shown that it is most efficient cycle for converting a given amount of thermal energy into work.

A system undergoing a Carnot cycle is called a Carnot heat engine.

Stages of the Carnot cycle:



1. Reversible isothermal expansion of the gas at hot temperature, T_1 (isothermal heat addition). During this step (1 to 2) the gas is allowed to expand and it does work on the surrounding. The gas expansion is propelled by absorption of quantity Q_1 at heat from the high temperature T_1.

2. Reversible adiabatic expansion of the gas. For this step (2 to 3) on figure, the gas continues to expand, working on surrounding. The gas expansion causes it to cool to the cold temperature T_2.
3. Reversible isothermal compression of the gas at the "cold" temperature T_2 (isothermal heat rejection). The process is shown by 3 → 4. Now the surroundings do work on the gas, causing quantity Q_2 of heat to flow out of the gas to the low temperature reservoir.
4. Adiabatic compression of the gas (4 to 1). During this step, the surrounding do work on the gas, compressing it and cause the temperature to rise to T_1. At this point the gas in the same state as at start at step 1.

Efficiency of Carnot engine:

$$\eta = \frac{W}{Q_1}$$

W is the work done during cycle and Q_1 is heat given to system.

$$W = W_1 + W_2 + W_3 + W_4$$

W_1 = work done during process 1 to 2 for isothermal process = $nRT_1 \ln \frac{V_2}{V_1}$

change in internal energy during the process $dU = 0$

$$Q_1 = W_1 = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$ (From first law of thermodynamics)

W_2 is work done during process 2 to 3 in adiabatic process.

$$dQ = 0 \qquad W_2 = \frac{nR(T_2 - T_1)}{1-\gamma}$$

W_3 = work done during process 3 to 4 isothermal compression.

$$W_3 = nRT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$Q_2 = W_3 \qquad dU = 0$$ (isothermal process)

W_4, the work done during the adiabatic process $4\,\text{to}\,1$, is given by

$$W_4 = \frac{nR(T_1 - T_2)}{1-\gamma}$$

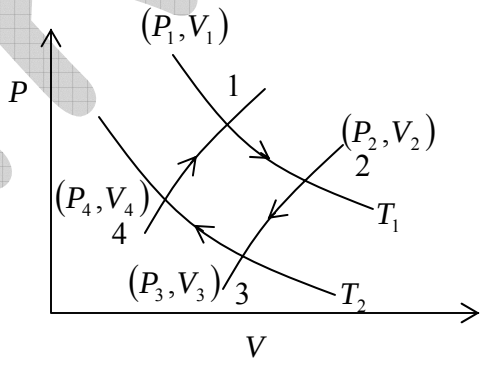
$$W_2 = -W_4$$

$$W = nRT_1 \ln\left(\frac{V_2}{V_1}\right) + nRT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$Q_1 = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\eta = \frac{W}{Q_1} = 1 + \frac{T_2}{T_1}\frac{\ln\left(\frac{V_4}{V_3}\right)}{\ln\left(\frac{V_2}{V_1}\right)} \quad \ldots.(i)$$

From the figure,



$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \ldots.(ii)$$

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \ldots.(iii)$$

Dividing equation (ii) by (iii) gives

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \ldots.(iv)$$

From equations (i) and (iv)

$$\eta = 1 - \frac{T_2}{T_1} \quad \ldots.(v)$$

For Carnot cycle, $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$

This gives $\eta = 1 - \frac{Q_2}{Q_1}$ $\ldots.(vi)$

Example: An ideal gas engine operator in a cycle which when represent on a *P-V* diagram is a rectangle. If we call P_1, P_2 and the lower and higher pressures respectively and V_1, V_2 as lower and higher volume respectively.

(a) Calculate the work done in complete cycle

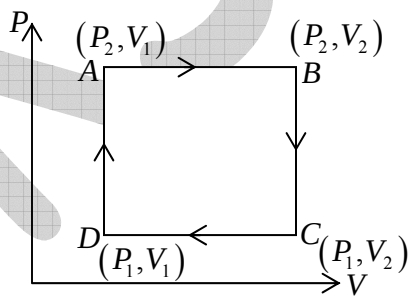
(b) indicate in which parts of the cycle heat is absorbed and in which part librated.

(c) Calculate the quantity of heat following into the gas in one cycle

(d) show that efficiency of the engine is

$$\eta = \frac{\gamma - 1}{\frac{\gamma P_2}{P_2 - P_1} + \frac{V_1}{V_2 - V_1}}$$

Solution: work done drawing $AB = P_2(V_2 - V_1)$



Heat absorbed = $nC_p\Delta T$

$$= nR\frac{\gamma}{\gamma - 1}(T_2 - T_1) = \frac{\gamma}{\gamma - 1}(P_2V_2 - P_2V_1)$$

$$= \frac{\gamma}{\gamma - 1}P_2(V_2 - V_1)$$

$V_2 > V_1$ so heat absorbed in the process.

In process B-C isochoric process

$W_{B-c} = 0$

$dQ = dU$

$nC_v\Delta T$

$$\frac{n}{\gamma - 1}R\Delta T = \frac{V_2}{\gamma - 1}(P_1 - P_2)$$

$P_1 < P_2$ heat rejected

In process C-D isobaric process

$W_{C-D} = P_1(V_1 - V_2)$

Heat exchange during the process

$$Q_{C\to D} = \frac{\gamma}{\gamma-1} P_1 (V_1 - V_2)$$

$V_1 < V_2$ so heat is rejected

In process D $\to$ A isochoric process

$$W_{D\to A} = 0$$

Heat exchange during the process

$$nC_v \Delta T = \frac{nR\Delta T}{\gamma-1} = \frac{V_1 (P_2 - P_1)}{\gamma-1}$$ heat absorbed.

(a) Work done = $P_2 (V_2\text{-}V_1) + P_1(V_1 - V_2)$

$$W = (P_2 - P_1)(V_2 - V_1)$$

(b) Heat absorbed $\frac{\gamma}{\gamma-1} P_2 (V_2 - V_1) + \frac{V_1}{\gamma-1}(P_2 - P_1)$

(c) Heat flowing into the cycle

$$\frac{\gamma P_2 (V_2 - V_1)}{\gamma-1} + \frac{V_2}{\gamma-1}(P_1 - P_2) + \frac{\gamma}{\gamma-1} P_1 (V_1 - V_2) + \frac{\gamma}{\gamma-1} V_1 (P_2 - P_1)$$

$$= \frac{\gamma}{\gamma-1}(V_2 - V_1)(P_2 - P_1) + \frac{1}{\gamma-1}(P_1 - P_2)\cdot(V_2 - V_1)$$

$$= \frac{\gamma}{\gamma-1}(V_2 - V_1)(P_2 - P_1) - \frac{1}{\gamma-1}(P_2 - P_1)(V_2 - V_1)$$

$$(P_2 - P_1)(V_2 - V_1)\left[\frac{\gamma}{\gamma-1} - \frac{1}{\gamma-1}\right] = (P_2 - P_1)(V_2 - V_1)$$

$$dQ = dW$$

(d) Efficiency = $\frac{W}{Q_{\text{absorbed}}} = \frac{(P_2 - P_1)(V_2 - V_1)}{\frac{\gamma P_2 (V_2 - V_1)}{\gamma-1} + \frac{V_1 (P_2 - P_1)}{\gamma-1}}$

Therefore, $\eta = \frac{\gamma-1}{\gamma \frac{P_2}{P_2 - P_1} + \frac{V_1}{V_2 - V_1}}$

4.3 Entropy

Entropy is an extensive thermodynamic property that is measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Thermodynamic entropy is a non-conserved state function. For Isolated systems entropy never decreases. In statistical mechanics, entropy is a measure of the number of ways in which a system may be arranged, often taken to be a measure of 'disorder' (the higher the entropy the higher the disorder).

The infinitesimal change in the entropy (dS) of a system is the infinitesimal transfer of heat energy (δQ) to a closed system driving a reversible process, divides by temperature (T) of the system.

$$\Delta S = \int \frac{\delta Q}{T}$$

It has unit Joule/Kelvin or $dS = \int \frac{\delta Q}{T}$

Law of thermodynamics and entropy:

According to first law of thermodynamics

$$\delta Q = dU + PdV$$

From definition of Entropy

$$\Delta S = \frac{\delta Q}{T} \Rightarrow \delta Q = T\Delta S \Rightarrow TdS$$

$$TdS = dU + pdV$$

4.3.1 Inequality of Clausius

Consider an irreversible cyclic engine working between T_1 and T_2. If reversible engine is operating between same temperature then from Carnot theorem.

Efficiency of irreversible (η_{ir}) will always smaller than efficiency of reversible engine(η_r).

$$\eta_{irr.} < \eta_{rev.}$$

$$\frac{Q_1^{irr} - Q_2^{irr}}{Q_1^{irr}} < \frac{Q_1^{rev} - Q_2^{rev}}{Q_1^{rev}}$$

$$1 - \frac{Q_2^{irr}}{Q_1^{irr}} < 1 - \frac{Q_2^{rev}}{Q_1^{rev}}$$

$$1 - \frac{Q_2^{irr}}{Q_1^{irr}} < 1 - \frac{T_2}{T_1}$$

$$\frac{Q_2^{irr}}{T_2} > \frac{Q_1^{irr}}{T_1}$$

F_0 irreversible cyclic Engine

$$\frac{Q_1^{irr}}{T_1} - \frac{Q_2^{irr}}{T_2} < 0$$

or $$\oint \frac{\delta Q}{T} < 0$$

This relation is known as inequality of Clausius.

Example: Two Carnot Engines A and B are operated in series. The first one A receives heat at 900 K and rejects to a reservoir at temperature T K. The second engine, B, receives the heat rejected by the first Engine and in then rejects to a heat reservoir at 400 K.

Calculate the temperature T for the situation.

(a) The work outputs of the two engines are equal

(b) The efficiency of the two engines are equal.

For Engine A take in heat Q_1 at temperature T_1 and rejected heat Q at temperature T; and the engine B taken in heat Q at temperature T and reject heat Q_2 at temperature T_2.

Solution: (a) $W_A = Q_1 - Q$ $\qquad W_B = Q - Q_2$

$W_A = W_B$ $\qquad Q_1 - Q = Q - Q_2$

$$\frac{Q_1 - Q_2}{Q} = 2$$

$$\frac{Q_1}{Q} = \frac{T_1}{T} \quad \text{and} \quad \frac{Q_2}{Q} = \frac{T_2}{T}$$

$$\frac{Q_1 + Q_2}{Q} = \frac{T_1 + T_2}{T} \Rightarrow \frac{T_1 + T_2}{T} = 2 \qquad T = 650 \ \ K$$

Solution: (b) $\eta_A = \eta_B$

$$1 - \frac{T}{T_1} = 1 - \frac{T_2}{T}$$

$$T = (T_1 \cdot T_2)^{\frac{1}{2}} \qquad T = 600 \ \ K$$

Example: Calculate the charge in isothermal expansion from an initial volume V_i to volume V_f

Solution: For reversible process

$$TdS = dU + PdV$$

For isothermal process $dU = 0$

$$dS = \frac{PdV}{T}$$

$$P = \frac{nRT}{V}$$

$$dS = nR\int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \frac{V_f}{V_i}$$

Example: A mass of liquid at a temperature T_1 is mined with an equal mass of the same liquid at a lower temperature T_2. the system is thermally insulated.

(a) compute the entropy-change

(b) show that it is necessarily positive.

Solution: Let c be the specific heat of the liquid. On the mining equal mass m of the same liquid at temperature T_1 and T_2 let $(T_1 > T_2)$.

Let T be the equilibrium temperature at minute.

$$mc(T_1 - T) = mc(T - T_2)$$

$$T = \frac{T_1 + T_2}{2}$$

$\Delta S_1 = \int_{T_1}^{T} \frac{\delta Q}{T}$ Entropy change of hotter liquid to cool from T_1 to T

$$\Delta S_1 = mc\int_{T_1}^{T} \frac{dT}{T} = mc \ln \frac{T}{T_1}$$

$\Delta S_2 \Rightarrow$ Entropy change of hotter liquid to heat from T_2 to T

$$\Delta S_2 = mc \ln \frac{T}{T_2}$$

ΔS = Entropy change of the system.

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= mc \ln \frac{T^2}{T_1 T_2} = mc \ln \left(\frac{\frac{T_1 + T_2}{2}}{\sqrt{T_1 T_2}} \right)^2 = 2mc \ln \frac{\frac{T_1 + T_2}{2}}{\sqrt{T_1 T_2}}$$

(b) we know arithmetic mean is greater than geometric mean.

$$AM > G.M.$$

So $\frac{T_1 + T_2}{2} > \sqrt{T_1 T_2}$ So $\Delta S > 0$

Example: Compute the change in entropy when ice melt into steam. It is given that L_1 is latent heat of fusion, c is specific heat at water and L_2 latent heat at vaporization.

Solution: Assume T_1 be the Kelvin temperature at which ice melts into water and T_2 the Kelvin temperature at which water is boiled to steam.

ΔS_1 is entropy change when ice is converted into water

$$\Delta S_1 = \frac{mL_1}{T_1}$$

ΔS_2 Entropy change when water is heated from T_1 to T_2

$$\Delta S_2 = mc\int_{T_1}^{T_2}\frac{dT}{T}$$

$$\Delta S_2 = mc\ln\frac{T_2}{T_1}$$

ΔS_3 Entropy change when water change into vapors

$$\Delta S_3 = \frac{mL_2}{T_2}$$

Total change in entropy $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{mL_1}{T_1} + mc\ln\frac{T_2}{T_1} + \frac{mL_2}{T_2}$

MCQ (Multiple Choice Questions)

Q1. Two Carnot engines A and B are operating between the same source and the same sink. Engine A uses an ideal gas as the working fluid while engine B uses Van der Waals' gas as the working fluid. Which one of the following is correct?

(a) The efficiency of engine A is less than that of engine B

(b) The efficiency of engine A is equal to that of engine B

(c) The efficiency of engine A is more than that of engine B

(d) No comparison can be made

Q2. A heat engine converts a given quantity of heat into work with maximum efficiency during which one of the following processes?

(a) Isobaric process (b) Isochoric process

(c) Isoenthalpic process (d) Isothermal process

Q3. If heat Q is added reversibly to a system at temperature T and heat Q' is taken away from it reversibly at temperature T', then which one of the following is correct?

(a) $\frac{Q}{T}-\frac{Q'}{T'}=0$

(b) $\frac{Q}{T}-\frac{Q'}{T'}>0$

(c) $\frac{Q}{T}-\frac{Q'}{T'}<0$

(d) $\frac{Q}{T}-\frac{Q'}{T'}=$ change in internal energy of the system

Q4. The temperature of water (mass, m) increases from T_1 to T_2. If c is the specific heat capacity of water, then the total increase in entropy of water is given by:

(a) $mc(T_2-T_1)$ (b) $mc\log_e\left(\frac{T_1}{T_2}\right)$

(c) $mc(T_1-T_2)$ (d) $mc\log_e\left(\frac{T_2}{T_1}\right)$

Q5. Consider the following that take place in Carnot cycle:

1. Adiabatic expansion
2. Adiabatic compression
3. Isothermal expansion
4. Isothermal compression

The correct sequence of the above processes is:

(a) 1, 3, 4, 2 (b) 3, 1, 2, 4

(c) 3, 1, 4, 2 (d) 1, 3, 2, 4

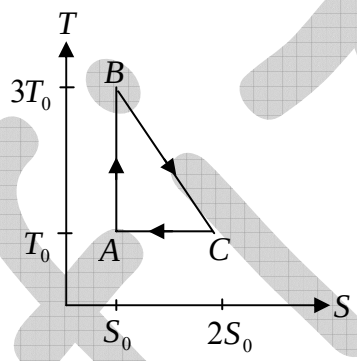
Q6. The change in entropy of the melting of 1kg of ice at $0^0 C$ is

(a) $3.66\ J/K$ (b) $15.31\ J/K$

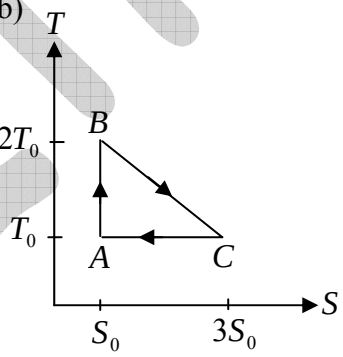
(b) $12.3\times10^2\ J/K$ (d) $1.14\times10^6\ J/K$

Q7. Which one of the following reversible cycles, represented by right angled triangles in a T-S diagram, is the least efficient?

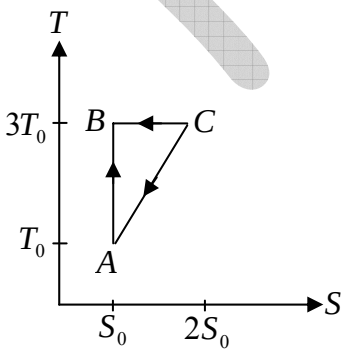
(a)



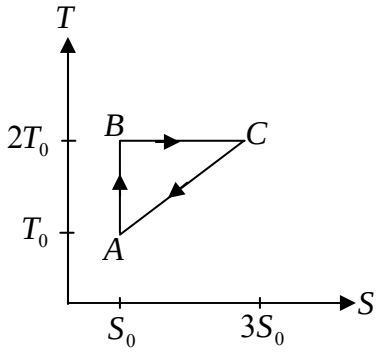
(b)



(c)



(d)



Q8. One mole of an ideal gas is carried from temperature T_1 and molar volume V_1 to T_2, V_2. Then the change in entropy is given by

(a) $\Delta S = R \ln \frac{V_2}{V_1}$ (b) $\Delta S = C_V \ln \frac{T_2}{T_1}$

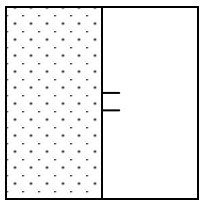
(c) $\Delta S = C_v \ln \frac{T_2}{T_1} - R \ln \frac{V_2}{V_1}$ (d) $\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

Q9. Consider an engine working in a reversible cycle and using an ideal gas with constant heat capacity C_p as the working substance. The cycle consists of two processes at constant pressure, joined by two adiabatic as shown in fig . Then the efficiency of this engine in terms of p_1, p_2 is given by

(a) $\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$ (b) $\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{1}{\gamma}}$

(c) $\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}}$ (d) $\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma}{\gamma-1}}$

Q10. An insulated chamber is divided into two halves of volumes. The left half contains an ideal gas at temperature T_0 and the right half is evacuated. A small hole is opened between the two halves, allowing the gas to flow through and the system comes to equilibrium. No heat is exchanged with the walls.



(a) During the process work done is zero but change in entropy of gas as well as universe $\Delta S = 0$

(b) During the process work done is not zero but change in entropy of gas $\Delta S = 0$ and change in entropy of universe $\Delta S > 0$

(c) During the process work done is zero but change in entropy of gas as well as universe $\Delta S > 0$

(d) During the process work done is not zero but change in entropy of gas $\Delta S > 0$ as well as universe $\Delta S > 0$

Q11. Each of the two isolated vessels, A and B of fixed volumes, contains N molecules of a perfect monatomic gas at a pressure P. The temperatures of A and B are T_1 and T_2, respectively. The two vessels are brought into thermal contact. At equilibrium, the change in entropy is

(a) $\frac{3}{2}Nk_B \ln\left[\frac{T_1^2+T_2^2}{4T_1T_2}\right]$

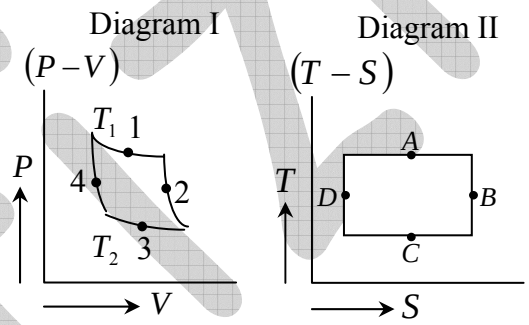
(b) $\frac{3}{2}Nk_B \ln\left(\frac{T_2}{T_1}\right)$

(c) $\frac{3}{2}Nk_B \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$

(d) $2Nk_B$

MSQ (Multiple Select Questions)

Q12. In diagram 1 Carnot cycle is represented in PV diagram while in Diagram II 1 Carnot cycle is represented in TS diagram



Which one of the following is correct?

(a) 1 and A is isothermal expansion and heat is given into the system

(b) B is adiabatic compression

(c) In process 3 heat is rejected by system

(d) Work done during 4 and B are same in magnitude and opposite to sign

Q13. Consider the following statements regarding the characteristics of entropy are correct

(a) Entropy is a measure of disorder.

(b) Entropy changes during a reversible adiabatic process.

(c) Entropy of a system decreases in all irreversible processes.

(d) Change in entropy for a complete reversible thermodynamic cycle is zero

Q14. Consider the following statements regarding transition of a system from one thermodynamic state another which of the following is correct

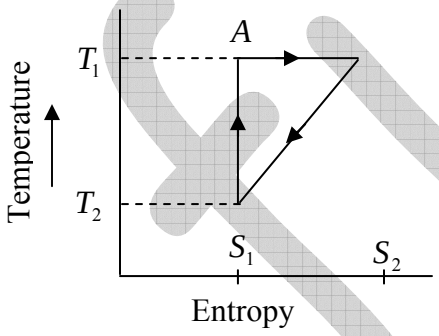
(a) The heat absorbed by it along any reversible path independent of the path.

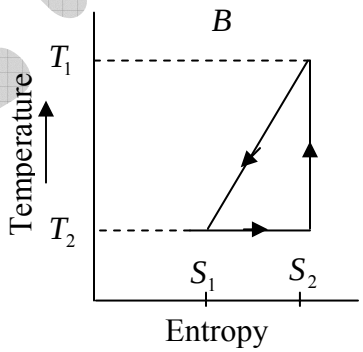
(b) The change of entropy of the system in a reversible : process is independent of the path.

(c) The change of entropy of the system in a irreversible process is also independent of the path.

(d) The heat absorbed by it along any irrereversible path independent of the path.

Q15. The temperature entropy diagrams of two engines A and B working between the same temperature T_1 and T_2 of the source and the sink respectively are shown in the given figures.





The efficiency of A:

(a) is less than that of B

(b) is equal to that of B

(c) is greater than that of B

(d) and B cannot be compared on the basis of data given in the diagrams

Q16. Which of the the following statements are correct

(a) The entropy change during a reversible adiabatic process is zero

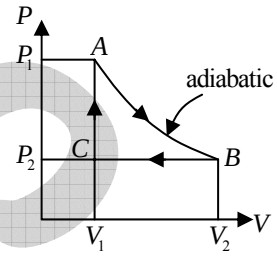
(b) Entropy is a state function

(c) The entropy of a thermally isolated system never decreases

(d) The entropy change during an reversible adiabatic process is zero.

Q17. An ideal gas is expanded adiabatically from (P_1,V_1) to (p_2,V_2). Then it is compressed isobarically to (P_2,V_1). Finally the pressure is increased to P_1 at constant volume V_1 then which of the following is correct?

(a) the $P-V$ indicator diagram is given by fig



(b) the work done in the cycle is $W=\frac{1}{1-\gamma}\left(P_2V_2-P_1V_1\right)+P_2\left(V_2-V_1\right)$

(c) heat will absorb in isochoric process

(d) the efficiency of the cycle is $\eta=1-\gamma\dfrac{\frac{V_2}{V_1}-1}{\frac{p_1}{p_2}-1}$

Q18. Consider an arbitrary heat engine which operates between reservoirs, each of which has the same finite temperature-independent heat capacity c. The reservoirs have initial temperatures T_1 and T_2, where $T_2>T_1$, and the engine operates until both reservoirs have the same final temperature T_3. Then which of the following statements are correct

(a) The change of entropy is given by $\ln\dfrac{T_3^2}{T_1T_2}$.

(b) In general $T_3\le\sqrt{T_1T_2}$

(c) In general $T_3\ge\sqrt{T_1T_2}$

(d) The maximum work done is given by $W_{\max}=c\left(\sqrt{T_1}-\sqrt{T_2}\right)^2$

Q19. Which of the statements are correct?

(a) A mole of an ideal gas undergoes a reversible isothermal expansion from volume V_1 to $2V_1$.Then change in entropy of the gas is $RT\ln 2$ and there is no change in entropy of the universe .

(b) A mole of an ideal gas undergoes a reversible isothermal expansion from volume V_1 to $2V_1$.Then change in entropy of the gas is $RT\ln 2$ and change in entropy of the universe is $RT\ln 2$

(c) A mole of an ideal gas undergoes free isothermal expansion from volume V_1 to $2V_1$.Then change in entropy of the gas is $RT\ln 2$ and there is no change in entropy of the universe

(d) A mole of an ideal gas undergoes free isothermal expansion from volume V_1 to $2V_1$.Then change in entropy of the gas is $RT\ln 2$ and change in entropy of the universe is $RT\ln 2$

Q20. A body of constant heat capacity C_P and a temperature T_i is put into contact with a reservoir at temperature T_f . Equilibrium between the body and the reservoir is established at established at constant pressure. Assume $T_f > T_i$. Then

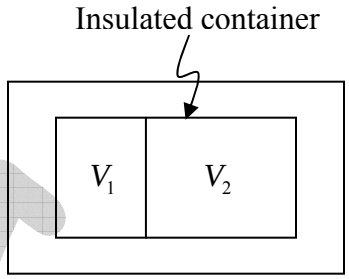
(a) Change of entropy of the body is $C_p \ln \frac{T_f}{T_i}$

(b) The change of entropy of the heat source is $\frac{C_p\left(T_i - T_f\right)}{T_f}$

(c) If $T_f > T_i$ then the change in entropy of universe $\Delta S > 0$

(d) If $T_f < T_i$ then change of entropy of universe is $\Delta S < 0$

Q21. n mole of an ideal gas is originally confined to a volume V_1 in an insulated container of volume V_1+V_2. The remainder of the container is evacuated. The partition is then removed and the gas expands to fill the entire container. If the initial temperature of the gas was T



(a) Then which of the following statement is correct

(b) The temperature remain constant T

(c) The work done during the process is $nRT\ln\left(\frac{V_1+V_2}{V_1}\right)$

(d) The change entropy of gas in the process is $nR\ln\left(\frac{V_1+V_2}{V_1}\right)$

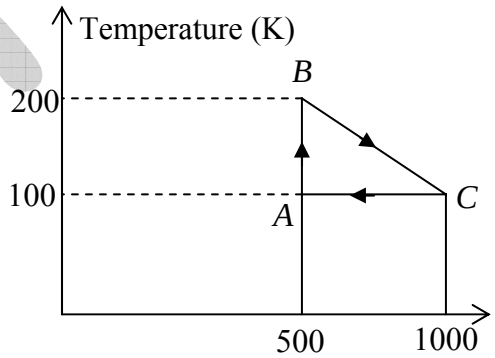
The change in entropy of universe during the process is $nR\ln\left(\frac{V_1+V_2}{V_1}\right)$

NAT (Numerical Answer Type Questions)

Q22. A Carnot engine has an efficiency of $\frac{1}{6}$. On reducing the sink temperature by $65°C$, the efficiency becomes $\frac{1}{3}$. The source temperature is given by ……^0K

Q23. A Carnot engine whose low-temperature reservoir is at 27^0C has an efficiency 37.5%.The high-temperature reservoir is ……^0C

Q24. In the given $T-S$ diagram, the efficiency is given by ……..% (Answer must be in two decimal point).



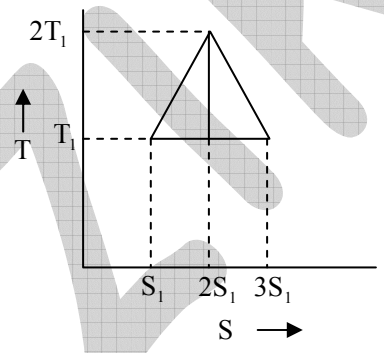
Q25. An ideal gas is confined to a cylinder by a piston. The piston is slowly pushed in so that the gas temperature remains at $20^0 C$. During the compression, $730\,J$ work is done on the gas. the entropy change by the gas is …….. J/K

Q26. 10 g of ice at $0°C$ is slowly melted to water at $0°C$. The latent heat of melting is 80 cal/g. The change in entropy is nearly ……. cal/K

Q27. If a capacitor of $1\mu F$ charged to a potential of $300V$ is charged, a resistor kept at room temperature, then the entropy change of the universe in……. $\times 10^{-4}$ J/K

Q28. One kg of H_2O at 0^oC is brought in contact with a heat reservoir at 100^oC. When the water has reached 100^oC Then the change in entropy of the universe is …… J/K (specific heat of water $C_{H_2O} = 4.18\,J/g$)

Q29. A reversible engine cycle is shown in the following T -S diagram. The efficiency of the engine is ……..%



Solution

MCQ (Multiple Choice Questions)

Ans. 1: (b)

Solution: The efficiency of a Carnot working between temperature limits T_1 and T_2 is given as

$$\eta = 1 - \frac{T_2}{T_1}$$

$T_1 \rightarrow$ absolute temperature of source

$T_2 \rightarrow$ absolute temperature of sink

Since, efficiency does not depend on -working substance hence the efficiency of both engines A and B are same

Ans. 2: (c)

Solution: The first law of thermodynamics

$$dQ = dU + PdV$$

The maximum efficiency can be obtained, if process is isoenthalpic.

Ans. 3: (a)

Solution: For a reversible process the change in entropy is zero.

$$\Rightarrow \quad dS = 0$$

$$\Rightarrow \quad \frac{Q_1}{T_1} - \frac{Q'}{T'} = 0$$

Ans. 4: (d)

Solution: The change in entropy of a system is given as $dS = \int_{T_1}^{T_2} \frac{\delta Q}{T}$

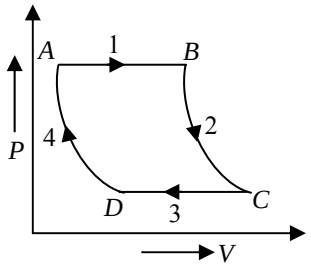
If δQ amount of heat is given to water then T_1 change in temperature dT is given as

$$\delta Q = mcdT$$

$$dS = \int_{T_1}^{T_2} \frac{mcdT}{T} = mc \log_e \frac{T_2}{T_1}$$

Ans. 5: (c)

Solution:



AB $\rightarrow$ isothermal expansion

BC $\rightarrow$ adiabatic expansion

CD $\rightarrow$isothermal compression

DA $\rightarrow$ adiabatic compression

Ans. 6: (c)

Solution: The change in entropy is given as

$$dS = \frac{\delta Q}{T}$$

here, $\delta Q = mL$, L is latent heat

$$= 1000 \times 80 \Rightarrow \delta Q = 80000 \quad cal$$

$$\Rightarrow \qquad \delta Q = 80000 \times 4.2\ J \qquad \text{(ii)}$$

$$T = 273\ K$$

so, $dS = \frac{80000 \times 4.2}{273} J/K = 12.3 \times 10^2\ J/K$

Ans. 7: (d)

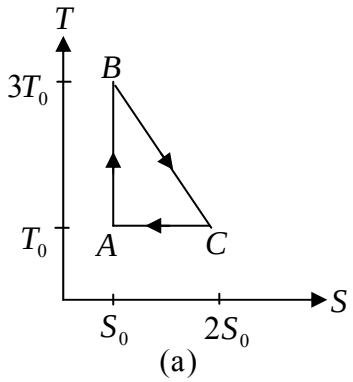
Solution: Efficiency $\eta = \frac{W}{Q_1}$

In a)

$$W = \frac{1}{2}(3T_0 - T_0)(2S_0 - S_0) = T_0 S_0$$

$$Q_1 = \frac{1}{2}(3T_0)(2S_0 - S_0) = 1.5 T_0 S_0$$

$$\eta = \frac{W}{Q_1} = 66\%$$



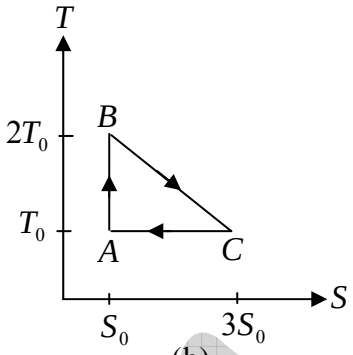
(a)

In (b)

$$W = \frac{1}{2}(2T_0 - T_0)(3S_0 - S_0) = T_0S_0$$

$$Q_1 = \frac{1}{2}(2T_0)(3S_0 - S_0) = 2T_0S_0$$

$$\eta = \frac{W}{Q_1} = 50\%$$



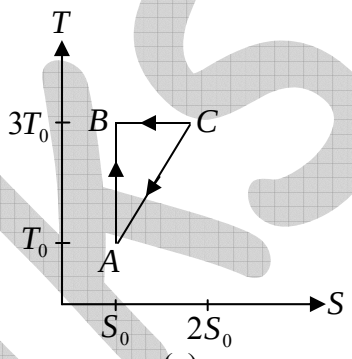
(b)

In (c)

$$W = \frac{1}{2}(3T_0 - T_0)(2S_0 - S_0) = T_0S_0$$

$$Q_1 = (3T_0)(2S_0 - S_0) = 3T_0S_0$$

$$\eta = \frac{W}{Q_1} = 33\%$$



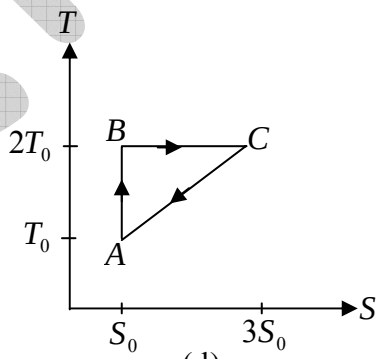
(c)

In (d)

$$W = \frac{1}{2}(2T_0 - T_0)(3S_0 - S_0) = T_0S_0$$

$$Q_1 = (2T_0)(3S_0 - S_0) = 4T_0S_0$$

$$\eta = \frac{W}{Q_1} = 25\%$$



(d)

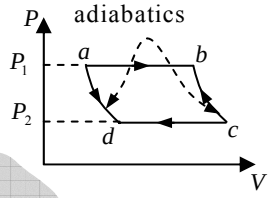
Ans. 8: (d)

Solution: From $dS = \frac{1}{T}(dU + PdV) = \frac{1}{T}(C_v dT + PdV)$ and $PV = RT$

We obtain $\Delta S = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$

Ans. 9: (a)

Solution: In the cycle, the energy the working substance absorbs from the source of higher temperature is $Q_{ab} = C_p\left(T_b - T_a\right)$.The energy it gives to the source of lower temperature is $Q_{reject} = C_p\left(T_c - T_d\right)$. Thus



$$\eta = 1 - \frac{Q_{reject}}{Q_{ab}} = 1 - \frac{T_c - T_d}{T_b - T_a}$$

form the equation of state $pV = nRT$ and the adiabatic equations

$$P_2V_d^{\gamma} = P_1V_a^{\gamma}, \quad P_2V_c^{\gamma} = P_1V_b^{\gamma} \qquad \text{we have} \quad \eta = 1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Ans. 10: (c)

Solution: After a hole has been opened, the gas flows continuously to the right side and reaches equilibrium finally. During the process, internal energy of the system E is unchanged. Since E depends on the temperature T only for an ideal gas, the equilibrium temperature is still T_0 so from first law of thermodynamics work done is zero but process is irreversible so change in entropy of gas as well as universe is $\Delta S > 0$

Ans. 11: (c)

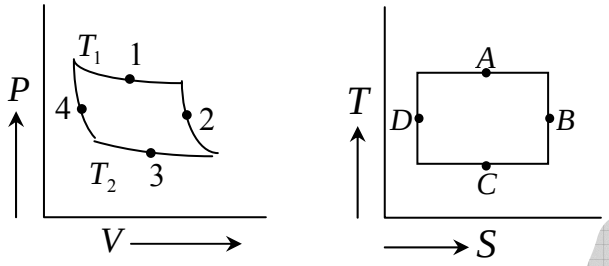
Solution: Final temperature of each vessel at equilibrium is $T = \frac{T_1 + T_2}{2}$

$$\Delta S = \int_{T_1}^{T} \frac{C_V dT}{T} + \int_{T_2}^{T} \frac{C_V dT}{T} = \frac{3}{2} \mathrm{N} k_B \ln\left[\frac{\left(\mathrm{T}_1 + \mathrm{T}_2\right)^2}{4\mathrm{T}_1\mathrm{T}_2}\right] \quad \text{where } C_V = \frac{3K_B}{2} \text{ for monatomic gas}$$

MSQ (Multiple Select Questions)

Ans. 12: (a), (c) and (d)

Solution:



Path 1: Expansion of constant temperature and heat is absorbed because $dQ = +ve$ hence S will increase Corresponding to A.

Path 2: Adiabatic expansion means S is constant Corresponding to B.

Path 3: Isothermal compression $dQ = -ve$ so heat will reject S is decrease corresponding to C.

Path A and path B are isoentropic process so work done is dependent on points but direction of both the case will opposite .

Ans. 13: (a) and (d)

Solution: Entropy is function of no of microstate which will measurement of disorderness

For thermodynamic process $dS \geq 0$ and for reversible process $dS = 0$.

Ans. 14: (b) and (c)

Solution: The entropy is point function and perfectly differential so it is path independent

Ans. 15: (a)

Solution: The efficiency is defined as

$$\eta = \frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1}$$

Ans. 16: (a), (b), (c) and (d)

Solution: Entropy:

where $\delta Q \rightarrow$ amount of used heat in reversible adiabatic process $\delta Q = 0$

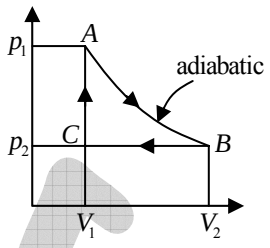
It is a state function and is defined as $dS = \frac{\delta Q}{T}$ is exact differential so it is state function

If this taken in by a system then change in entropy is positive and so entropy of the system increases.

The entropy change during an reversible adiabatic process is zero.

Ans. 17: (a), (b) and (d)

Solution: (a) The cycle is shown in the figure



(b)The work the system does in the cycle is

$$W = \oint PdV = \int_{AB} PdV + P_2\left(V_1 - V_2\right)$$

Because AB is adiabatic and an ideal gas has the equations $pV = nkT$ and $C_p = C_v + R$, we get

$$\int_{AB} PdV = -\int_{AB} C_v dT = -C_v\left(T_2 - T_1\right) = \frac{1}{1-\gamma}\left(P_2V_2 - P_1V_1\right)$$

(c) During the CA part of the cycle the gas absorbs heat which is isochoric

$$Q = \int_{CA} TdS = \int_{CA} C_v dT = C_v\left(T_1 - T_2\right) = \frac{1}{1-\gamma}V_1\left(P_2 - P_1\right)$$

(d) Hence, the efficiency of the engine is

$$\eta = \frac{W}{Q} = 1 - \gamma\frac{\frac{V_2}{V_1} - 1}{\frac{P_1}{P_2} - 1}$$

Ans. 18: (a), (c) and (d)

Solution: (a) The increase in entropy of the total system is

$$\Delta S = \int_{T_1}^{T_3}\frac{cdT}{T} + \int_{T_2}^{T_3}\frac{cdT}{T} = c\ln\frac{T_3^2}{T_1T_2} \geq 0$$

(c) Thus $T_3^2 \geq T_1T_2$, or $T_3 \geq \sqrt{T_1T_2}$

(d) The maximum amount of work can be obtained using a reversible heat engine, for which $\Delta S = 0$.

$$W_{\max} = c\left(T_1 + T_2 - 2T_{3\min}\right) = c\left(T_1 + T_2 - 2\sqrt{T_1T_2}\right) = c\left(\sqrt{T_1} - \sqrt{T_2}\right)^2$$

Ans. 19: (a) and (d)

Solution: In the process of isothermal expansion, the external work done by the system is

$$W = \int_{V_1}^{2V_1} PdV = RT\int_{V_1}^{2V_1} \frac{dV}{V} = RT\ln 2$$

Because the internal energy does not change in this process the work is supplied by the heat absorbed from the external world. Thus the increase of entropy of the gas is

$$\Delta S_1 = \frac{\Delta Q}{T} = \frac{W}{T} = R\ln 2$$

The change in entropy of the heat source $\Delta S_2 = -\Delta S_1$ thus the total change in entropy of the universe is $\Delta S = \Delta S_1 + \Delta S_2 = 0$.

If it is a free expansion, the internal energy of the system is constant. As its final state is the same as for the isothermal process, the change in entropy of the system is also the same. In this case, the state of the heat source does not change, neither does its entropy. Therefore the change in entropy of the universe is $\Delta S = R\ln 2$.

Ans. 20: (a), (b) and (c)

Solution: We assume $T_i \neq T_f$ (because the change of entropy must be zero when $T_i = T_f$). The change of entropy of the body is

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln \frac{T_f}{T_i}$$

The change of entropy of the heat source is

$$\Delta S_2 = \frac{\Delta Q}{T_f} = \frac{C_p\left(T_i - T_f\right)}{T_f}$$

Therefore the total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = C_p\left(\frac{T_i}{T_f} - 1 + \ln\frac{T_f}{T_i}\right)$$

when $x > 0$ and $x \neq 1$, the function $f\left(x\right) = x - 1 - \ln x > 0$.

The change in entropy of universe during the process is $nR\ln\left(\frac{V_1+V_2}{V_1}\right)$

Ans. 21: (a), (c) and (d)

Solution: This is a process of adiabatic **free expansion** of an ideal gas. The internal energy does not change; thus the temperature does not change, that is, the final temperature is still T. From first law of thermodynamics the work done is zero . hence the process is irreversible and entropy is state function so one can choose path isothermal reversible process . so change in entropy in isothermal is $nR\ln\left(\frac{V_1+V_2}{V_1}\right)$ which is equal to change in entropy of gas as well as universe .

NAT (Numerical Answer Type Questions)

Ans. 22: 390

Solution: If T_2 is Sink temperature and T_1 Source temperature

Then, efficiency is given $\eta=\frac{T_1-T_2}{T_1}$

Case 1: $\frac{1}{6}=1-\frac{T_2}{T_1} \Rightarrow T_2=\frac{5}{6}T_1$

Case 2: If T_2 is reduced by $65°C$, then $T_2'=T_2-65$

$$\eta'=1-\frac{T_2'}{T_1}$$

$$\Rightarrow \quad \frac{1}{3}=1-\frac{T_2-65}{T_1} \Rightarrow \frac{1}{3}=1-\frac{T_2}{T_1}+\frac{65}{T_1}$$

$$\frac{1}{3}=1-\frac{5}{6}+\frac{65}{T_1} \Rightarrow T_1=65\times 6=390\ {}^0K$$

Ans. 23: 207

Solution: If T is temperature of source, T is the temperature of the smk then efficiency

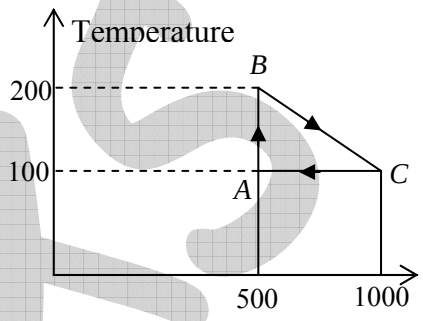
$$\eta = 1 - \frac{T_2}{T_1} \qquad \Rightarrow \frac{37.5}{100} = 1 - \frac{300}{T_1}$$

$$\frac{300}{T_1} = 1 - \frac{37.5}{100} = \frac{200 - 75}{200} \quad \Rightarrow T_1 = \frac{300 \times 8}{5} = 480$$

$$\Rightarrow \qquad t = 480 - 273 \quad = 207^0 C$$

Ans. 24: 33.33

Solution:



$$\eta = \frac{W}{Q_1}$$

$$W = \frac{1}{2}.(200 - 100)(1000 - 500) = 25000$$

$$Q_1 = 50{,}000 + \left(\frac{1}{2} \times 500 \times 100\right) = 75{,}000\ J$$

$$\eta = \frac{W}{Q_1} = 33.33\%$$

Ans. 25: -1.85

Solution: If Q amount of heat is taken by or given to (a) system at temperature T then change in entropy is given as

$$dS = \frac{\delta Q}{T}$$

By first law of thermodynamic

$$\delta Q = dU + \delta W$$

According to question, since temperature is constant so no change in internal energy

$$\Rightarrow \qquad dU = 0$$

and work of $730J$ is done on the system $\Rightarrow \qquad \delta Q = -730\,J$

From first law of thermodynamics, $\delta Q = -0 + (-730) \Rightarrow \delta Q = -730 \quad J$

and $\quad T = 273 + 20 = 293\,K$

$$dS = \frac{\delta Q}{T} \quad = \frac{-730}{293} \quad = -1.85 J/K$$

Ans. 26: 2.9

Solution: The entropy is defined as

$$dS = \frac{\delta Q}{T}$$

Here, $\delta Q = ML = 10 \times 80 = 800\,\text{cal}$ and $T = 0 + 273 = 273\,\text{K}$

So, $dS = \frac{800}{273}\,\text{cal/K}$ $= 2.9\,\text{cal/K}$

Ans. 27: 1.5

Solution: The energy stored in capacitor $= \frac{1}{2}CV^2$

So, change in entropy is given $dS = \frac{\delta Q}{T} \Rightarrow$ $dS = \frac{CV^2}{2T}$

Here, $C = 10^{-6}F, V = 300Volt, T = 27 + 273 = 300K$

So, change in entropy $dS = \frac{10^{-6} \times (300)^2}{2 \times 300} = \frac{10^{-6} \times 9 \times 10^4}{2 \times 300} = 1.5 \times 10^{-4}\,J/K$

Ans. 28: 184

Solution: We assume the process is a reversible process of constant pressure. The change in entropy of the water is $\Delta S_{H_2O} = \int_{273}^{373} mC_{H_2O}\frac{dT}{T} = mC_{H_2O}\ln\left(\frac{373}{273}\right)$

we substitute $m = 1kg$, and $C_{H_2O} = 4.18\,J/g$ into it, and find

$$\Delta S_{H_2O} = 1305\,J/K$$

The change in entropy of the heat source is

$$\Delta S_{ha} = -\frac{|Q|}{T} = -1000 \times 4.18 \times \frac{100}{373} = -11121\,J/K$$

Therefore the change of entropy of the whole system is $\Delta S = \Delta S_{H_2O} + \Delta S_{ha} = 184\,J/K$

Ans. 29: 33

Solution: $W = \frac{1}{2}(2T_1 - T_1)(3S_1 - S_1) = T_1S_1$

$$Q = \frac{1}{2}(2T_1 - T_1)(3S_1 - S_1) + T_1(3S_1 - S_1) = T_1S_1 + T_1 2S_1 \quad = 3T_1S_1$$

$$\eta = \frac{W}{Q} = \frac{T_1S_1}{3T_1S_1} = .33 = 33\%$$

fiziks

Chapter - 5

Maxwell relation and Thermodynamic Potential

5.1 Maxwell Relations

$F = F(x, y)$ and if it is perfect differential then $dF = Mdx + Ndy$

Where $M = \left(\frac{\partial F}{\partial x}\right)_y$ and $N = \left(\frac{\partial F}{\partial y}\right)_x$ then M and N will satisfy the condition $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$

Maxwell relations are relationship between two derivatives of thermodynamic variables, and energy due to the equivalence of potential second derivative under a change of operation order $\frac{d^2F}{dx\,dy} = \frac{d^2F}{dy\,dx}$ where F is thermodynamic potential and x and y are two of its natural independent variables.

Maxwell relations are extremely important for two reasons.

First they show us that derivative of thermodynamic parameters are not all independent. This can serve as a consistency check in both experiments and in theoretical analysis.

Maxwell relations provide a method for expressing some derivative in other ways. This enables as to connect difficult to measure quantities to those which are readily accessible experimentally.

The measurement of entropy and chemical potential can not be directly measurable in lab but with the help of Maxwell relation there thermodynamic property can be determine theoretically.

For **Maxwell relation.**

Let us Legendre the independent variable as x, and y such that

$$U = U(x,y),\ S = S(x, y)\quad V = V(x, y)$$

So $$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dx$$

from first law of thermodynamic

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - p\left(\frac{\partial V}{\partial y}\right)_x$$

Hence U, V,and S are perfect differential.

Then $\left[\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right]_y$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right]_y$$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right]_y$$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right]_x = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left[\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right]_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\left[\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right]_x \quad \text{---(1)}$$

Similarly

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right]_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left[\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right]_y - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\left[\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right]_y \quad \text{---(2)}$$

Equating equation (1) and (2)

$$\left(\frac{\partial P}{\partial x}\right)_x\left(\frac{\partial V}{\partial y}\right)_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y \qquad \text{(A)}$$

Maxwell first relation:- put $x = T,\ y = V$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Maxwell Second Relation:- put $x = T,\ y = P$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell Third Relation:- put $x = S,\ y = V$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Maxwell Fourth Relation:- put $x = S,\ y = P$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Thermodynamic potential is a scalar function used to represent the thermodynamic state of system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886.

One main thermodynamic potential that has a physical interpretation is the internal energy. It is energy of configuration of a given system of conservative forces. Expression for all other thermodynamic energy potentials are drivable via Legendre transformation.

5.2 Different Types of Thermodynamic Potential and Maxwell Relation

Thermodynamic potentials are different form of energy which can be used in different thermodynamic process .thermodynamic potentials are path independent variables so they are perfect differential

If F is unique thermodynamic potential defined by variables x and y as $F = F(x, y)$ and if it is perfect differential then $dF = Mdx + Ndy$

Where $M = \left(\frac{\partial F}{\partial x}\right)_y$ and $N = \left(\frac{\partial F}{\partial y}\right)_x$ then M and N will satisfy the condition $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$

5.2.1 Internal Energy :- U and second from the first laws of thermodynamics

$$dU = TdS - PdV$$

from Legendre transformation

$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$ from given relation one can derive Maxwell relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

5.2.2 Enthalpy (H) the enthalpy is defined as $H = U + PV$

$$dH = dU + PdV + VdP$$

from Laws of thermodynamics

$$TdS = dU + PdV$$

$$dH = TdS + VdP$$

from Legendre transformation

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = P$$

The Enthalpy H is Extensive quantity, which can not be measured directly. Thus change in enthalpy is more useful.

ΔH is positive in endothermic reaction and negative in exothermic reaction.

From above relation one can derive Maxwell relation $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

ΔH of a system is equal to sum of non-mechanical work done on it and the heat supplied to it.

5.2.3 Helmholtz Free Energy (F) the Helmholtz free energy is defined $F = U - TS$

$$dF = dU - TdS - SdT$$

From laws of thermodynamics $dU = TdS - PdV$

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

From Legendre transformation

$$\left(\frac{\partial F}{\partial V}\right)_T = -P, \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

From above relation one can derive Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

The free Energy F, which is available energy for work in reversible isothermal process.

5.2.4 Gibbs Energy: *'G'* is defined as G = *H – TS*.

$$G = U + PV - TS$$

$$dG = dU + PdV - VdP - TdS - SdT$$

$$TdS - PdV + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

from Legendre transformation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

From above relation one can derive Maxwell relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Gibbs free energy is popularly as free enthalpy.

The Gibbs free energy is Maximum amount of nonexpanding work that can be exacted from a closed system.

The maximum will activated when the system is in reversible process.

Gibbs free energy is also treated as chemical potential.

In thermodynamics, chemical potential, as partial molar free energy, is a form of potential energy that can be absorbed or relived during a chemical reaction.

The chemical potential of a species in the minute can be defined the slope of the energy at system with respect to a change in the no of moles.

$$\mu = \left.\frac{dG}{dN}\right|_V$$

where μ is chemical potential, G is Gibbs energy and N is no of molecules

Example: Prove that internal energy U is given by

$$(a) U = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$$

$$(b)\ H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$$

Solution: (a) $F = U - TS = U = F + TS$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$U = F + T\left(\frac{-\partial F}{\partial T}\right)_V = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial(F/T)}{\partial T}\right)_V = \left(\frac{\partial(F/T)}{\partial 1/T}\right)_V$$

Solution: (b) $H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$

$$G = H - TS$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P\right)$$

$$= \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P$$

5.3 Application of Maxwell Relation

5.3.1 First $T - dS$ equation

Let T, and V are independent variable $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{put}\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$T \cdot dS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.$$

5.3.2 Second $T - dS$ Equation

Let T and P are independent variable $S = S(T, P)$.

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

From Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right) = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

5.3.3 Third *T-dS* Equation:

Let P,V are independent variable S = S (P,V)

$$dS = \left(\frac{\partial S}{\partial P}\right)_P dP + \left(\frac{\partial S}{\partial V}\right)_V dV$$

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_V dV$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$= C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

5.3.4 The First Energy Equation

Let T and V are independent variable U = U(T, V)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From first law of thermodynamics.

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Using Maxwell relation $T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$dU = C_v dT + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)dV$$

5.3.5 Second Energy Equation

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Using Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$ This is popularly known as second energy equation

Application of second energy equation

If U is function of independent variable of T and P.

$$U = U(T, P)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

Example: From relation $dU = TdS - PdV$

Derive Maxwell relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

Solution: $dU = TdS - PdV$ $\quad \left(\frac{\partial U}{\partial V}\right)_S = -P,\ \left(\frac{\partial U}{\partial S}\right)_V = T$

Hence U is exact differential

$$\left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_v = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

Example: A real gas which obey van der Waal's equation of state are kept in container which has temperature T_0 and volume V_0. if volume of container changes to V such that temperature of gas become T what is change in entropy?

Solution: Assume C_V is specific heat of constant volume

For van der Waal's gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

From first $T - dS$ equation

$$TdS = C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

$$dS = C_V \int_{T_0}^{T} \frac{dT}{T} + \int_{V_0}^{V} \frac{R}{(V - b)} dV$$

$$S = C_V \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{V - b}{V_0 - b}\right) + S_0$$

where S_0 is integration constant

Example: For Vander wall gases, prove that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$ where U is internal energy.

Solution: From first energy equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{-----(i)}$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$$ put the value of $\left(\frac{\partial P}{\partial T}\right)_V$ in equation (i)

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

Example: Prove that

(a) $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$

(b) $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

Solution: (a) we know $C_V = T\left(\frac{\partial S}{\partial T}\right)_v$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left[\frac{\partial^2}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\left[\frac{\partial^2}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V$$

using Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$ one can get $T\left[\frac{\partial^2}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V = T\left[\frac{\partial^2}{\partial T}\left(\frac{\partial P}{\partial T}\right)\right]_V$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

(b) $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = T\left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P$$

Use Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Example: If α_p is thermal expansivity at constant pressure and K_T isothermal compressibility then prove that

(i) $\left(\frac{\partial S}{\partial P}\right)_T = -V\alpha_p$

(ii) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_p}{K_T}$

(iii) $C_P - C_V = \frac{TV\alpha^2 P}{K_T}$

Solution: From Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right], \left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

(ii) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial T}{\partial V}\right)_P=-1$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial T}{\partial V}\right)_P}=\frac{-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{-\alpha}{K_T}$$

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV \qquad dS=\frac{C_V}{T}dT+\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P=\frac{C_V}{T}+\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad \frac{C_P}{T}=\frac{C_V}{T}+V\alpha_P\left(\frac{\partial S}{\partial V}\right)_T$$

Use Maxwell relation

$$\frac{C_P}{T}=\frac{C_V}{T}+V\alpha_P\left(\frac{\partial P}{\partial T}\right)_V \qquad \frac{C_P}{T}=\frac{C_V}{T}+V\alpha_P\left(\frac{\alpha_P}{K_T}\right)$$

$$C_P-C_V=\frac{TV\alpha_p^2}{K_T}$$

Example: Prove that

(a) $C_P-C_V=T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

(b) For the Vander Waal's gas prove that

$$C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$$

Solution: (a) $C_P-C_V=\left(\frac{\partial Q}{\partial T}\right)_P-\left(\frac{\partial Q}{\partial T}\right)_V$

$$=T\left(\frac{\partial S}{\partial T}\right)_P-T\left(\frac{\partial S}{\partial T}\right)_V \qquad \text{---- (A)}$$

$S=S(T,V)$

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \left(\frac{\partial S}{\partial T}\right)_P=\left(\frac{\partial S}{\partial T}\right)_V+\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Put the value of $\left(\frac{\partial S}{\partial T}\right)_P$ in equation (A)

$$C_P-C_V=T\left(\frac{\partial S}{\partial T}\right)_V+T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P-T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow C_P-C_V=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

$$=T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \because\left[\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V\right]$$

(b) For van der Waal's gas

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \qquad \text{---- (B)}$$

$$\left(P+\frac{a}{V^2}\right)=\frac{RT}{(V-b)} \quad \rightarrow \text{differentiate w.r.t. to T}$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{R}{V-b}$$

Differentiate (B) with respect to V

$$-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P=-\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P+\frac{R}{V-b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{\frac{R}{V-b}}{\frac{RT}{(V-b)^2}-\frac{2a}{V^3}}$$

Substituting the value $\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$ in equation

$$C_P-C_V=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad C_P-C_V=T\frac{\frac{R}{(V-b)}\left(\frac{R}{V-b}\right)}{\frac{RT}{(V-b)^2}-\frac{2a}{V^3}}$$

$$= \frac{R}{1-\left(\frac{2a}{V^3}\right)\frac{(V-b)^2}{RT}}$$

$$C_P - C_V = \frac{R}{1-\left(\frac{2a}{V^3}\right)\frac{V^2}{RT}} = R\left(1-\frac{2a}{RTV}\right)^{-1}, \quad C_P - C_V = R\left(1+\frac{2a}{RTV}\right)$$

Example: From $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

Prove $C_P - C_V = TE\alpha^2 V$ where E is bulk modulus of elasticity and α is coefficient of volume expansion.

Solution: Let $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

$$P = P(T,V)$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

For constant pressure $dP = 0$

$$\left(\frac{\partial P}{\partial T}\right)_V dT = -\left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$$

$$E = -V\left(\frac{\partial P}{\partial V}\right)_T \text{ and } \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = -T\frac{V}{V}\left(\frac{\partial P}{\partial V}\right)_T \frac{V^2}{V}\left(\frac{\partial V}{\partial T}\right)^2 = -T\left(\frac{E}{V}\right)V^2\alpha^2$$

$$C_P - C_V = -TVE\alpha^2$$

Example: If Helmholtz free energy for radiation is given by

$$F = -\frac{8\pi^5 K_B^4 T^4}{45h^3c^3}V$$

(a) What is radiation pressure

(b) If S entropy of system prove that specific heat at constant volume is given by $C_V = 3S$

Solution: (a) $dF = -SdT - PdV$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{8\pi^5 K_B^4 T^4}{45h^3c^3}$$

(b) $$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{32\pi^5 K_B^4}{45h^3c^3}VT^3$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\cdot 3\cdot\left(\frac{32\pi^5 K_B^4}{45h^3c^3}\right)VT^2 = 3\cdot\left(\frac{32\pi^2 K_B^4}{45h^3c^3}\right)VT^3$$

$$C_V = 3S$$

Example: The internal energy E of a system is given by $E = \frac{bS^3}{VN}$ where b is constant and other symbols have their used meaning.

(a) Find the temperature of system

(b) Find Pressure of system

Solution: From first law of thermodynamics

$$TdS = dU + PdV \qquad U = E = \frac{bS^3}{VN} \qquad dU = TdS - PdV$$

(a) $$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad T = \frac{3bS^2}{VN}$$

(b) $$P = -\left(\frac{\partial U}{\partial V}\right)_S \qquad P = -\left(-\frac{bS^3}{V^2N}\right) \qquad P = \frac{bS^3}{V^2N}$$

Example: Consider an Ideal gas where entropy is given by

$$S = \frac{n}{2}\left[\sigma + 5R\ln\frac{U}{n} + 2R\ln\frac{V}{n}\right]$$

where n = number of moles, R = universal gas constant, U = internal energy V = volume and σ = constant

(a) Calculate specific heat at constant pressure and volume

(b) Prove that internal energy is given by $U = \frac{5}{2}PV$

Solution: (a) From first law of thermodynamics

$$TdS = dU - PdV \;,\; dS = \frac{1}{T}dU - \frac{P}{T}dV \qquad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$$\frac{n}{2}\frac{5R}{U} = \frac{1}{T} \qquad U = \frac{5}{2}nRT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right) = \frac{5}{2}nR \Rightarrow C_P = C_V + R \Rightarrow C_P = \frac{7}{2}nR$$

(b) $$U = \frac{5}{2}nRT \quad \Rightarrow \quad \frac{U}{V} = \frac{5}{2}\frac{nRT}{V}$$

$$PV = nRT \quad \Rightarrow \quad V = \frac{nRT}{P}$$

$$\frac{U}{V} = \frac{5}{2}P \quad \Rightarrow \quad U = \frac{5}{2}PV$$

Example: Using the equation of state $PV = nRT$ and the specific heat per mole $C_v = \frac{3R}{2}$ for monatomic ideal gas

(a) Find Entropy of given system.

(b) Find free energy of given system

$$dU = nC_V dT, \qquad p = \frac{nRT}{V} \qquad C_V = \frac{3R}{2}$$

$$TdS = dU + PdV$$

$$dS = \frac{dU}{T} + \frac{p}{T}dV \qquad \text{or } ds = nC_V \frac{dT}{T} + nR\frac{dV}{V}$$

$$S = \frac{3}{2}NR\ln T + N\ln V + S_0 \text{ where } S_0 \text{ is constant}$$

(b) $F = U - TS$

$$= \frac{3nRT}{2} - \left(\frac{3nRT}{2}\ln T - nRT\ln V\right) + F_0 \text{ where } F_0 = T\cdot S_0 \text{ is again constant}$$

Example: From electromagnetic theory Maxwell found that the pressure P from an isotropic radiation equal to $\frac{1}{3}$ the energy density i.e. $P = \frac{1}{3}\frac{U}{V}$ where V is volume of the cavity using the first energy equation prove that

Energy density u is proportional to T^4.

Solution: $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_T - P$

$$P = \frac{1}{3}u \qquad u = \frac{U}{V}$$

$$= \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\left(\frac{\partial U}{\partial T}\right)_V \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{T}{3V}\left(\frac{\partial U}{\partial T}\right)_V - \frac{U}{3V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = u \qquad u = \frac{T}{3}\left(\frac{du}{dT}\right)_v - \frac{1}{3}u$$

$$T\frac{du}{dT} = 4u = \frac{du}{u} = 4\frac{dT}{T}$$

$$u \propto T^4 = u = \alpha T^4 \qquad \text{where } \alpha \text{ is a constant.}$$

MCQ (Multiple Choice Questions)

Q1. Which of the following is not a Maxwell's thermodynamic relation?

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(b) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(c) $\left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial V}{\partial S}\right)_P$

(d) $\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial S}{\partial T}\right)_P$

Q2. Which one of the following thermo dynamical relations is used for certain adiabatic changes, such as the sudden compression of a liquid or sudden -stretching of a rod?

(a) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

(b) $\left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T$

(c) $\left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T$

(d) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Q3. Which one of the Maxwell's thermodynamic relations given below leads to Clausius-Clapeyron equation?

(a) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(b) $\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P$

(c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(d) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Q4. Which of the following is correct if α is volume expansivity and other variables have usual meaning in thermodynamics .

(a) $\left(\frac{\partial C_P}{\partial P}\right)_T = -TV\alpha^2$

(b) $\left(\frac{\partial C_P}{\partial P}\right)_T = TV\alpha^2$

(c) $\left(\frac{\partial C_P}{\partial P}\right)_T = -\frac{TV}{\alpha^2}$

(d) $\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{TV}{\alpha^2}$

Q5. Which of the following can be derived by $S = S(T,V)$?

(a) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

(b) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dV$

(c) $TdS = C_V dT - T\left(\frac{\partial P}{\partial T}\right)_V dV$

(d) $TdS = C_P dT + T\left(\frac{\partial V}{\partial T}\right)_P dV$

Q6. Which of the following can be derived by $S = S(T,P)$?

(a) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ (b) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dV$

(c) $TdS = C_V dT - T\left(\frac{\partial P}{\partial T}\right)_V dV$ (d) $TdS = C_P dT + T\left(\frac{\partial V}{\partial T}\right)_P dV$

Q7. For an isolated thermodynamically system, P,V,T,U,S and F represent the pressure, volume, temperature, internal energy, entropy, and Helmholtz free energy respectively. Then the following relation is true

(a) $\left(\frac{\partial F}{\partial T}\right)_V = -S$ (b) $\left(\frac{\partial F}{\partial T}\right)_P = -S$

(c) $\left(\frac{\partial U}{\partial S}\right)_V = T$ (d) $\left(\frac{\partial U}{\partial V}\right)_V = -P$

Q8. Which of the following thermodynamic relation will give the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$?

(a) $dU = TdS - PdV$ (b) $dH = TdS + VdP$

(c) $dF = -SdT - PdV$ (d) $dG = -SdT + VdP$)

Q9. Which of the following is **not** an exact differential?

(a) dQ where Q heat absorbed (b) dU where U is internal energy

(c) dS where S is entropy (d) dF where S is entropy

Q10. Which among the following sets of Maxwell relations is correct? (U-internal energy, H-enthalpy, A-Helmholtz free energy and G-Gibbs free energy)?

(a) $T = \left(\frac{\partial U}{\partial V}\right)_S$ and $P = \left(\frac{\partial U}{\partial S}\right)_V$ (b) $V = \left(\frac{\partial H}{\partial P}\right)_S$ and $T = \left(\frac{\partial H}{\partial S}\right)_P$

(c) $P = -\left(\frac{\partial G}{\partial V}\right)_T$ and $V = \left(\frac{\partial G}{\partial P}\right)_S$ (d) $P = -\left(\frac{\partial A}{\partial S}\right)_T$ and $S = \left(\frac{\partial A}{\partial P}\right)_V$

Q11. When a system is held at constant temperature and pressure in a state of equilibrium, then it attains a minimum value of:

(a) internal energy (b) enthalpy

(c) Helmholtz energy (d) Gibb's free energy

Q12. Given that

H = the enthalpy of a system

T = absolute temperature and

S = entropy

$G = H - TS$ is the Gibbs function for the system

In the case of a reversible, isotherm and isobaric process:

(a) $G =$ constant

(b) $G > 0$ and changes with T

(c) $G < 0$ and changes with S

(d) G changes with both T and S

Q13. The Gibb's function G in thermodynamics is defined is

$$G = H - TS$$

where H is the enthalpy, T is the temperature and S is the entropy. In an isothermal, isobaric, reversible process, G:

(a) remains constant, but not zero (b) varies linearly

(c) varies non-linearly (d) is zero

Q14. The internal energy E of a system is given by $E = \frac{bS^3}{VN}$, where b is a constant and other symbols have their usual meaning. The temperature of this system is equal to

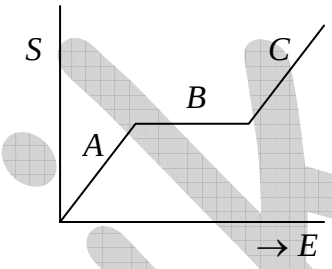
(a) $\frac{bS^2}{VN}$ (b) $\frac{3bS^2}{VN}$ (c) $\frac{bS^3}{V^2N}$ (d) $\left(\frac{S}{N}\right)^2$

Q15. The free energy of gas of N particles in a volume V and at a temperature T is $F = Nk_BT\ln\left[a_0V(k_BT)^{5/2}/N\right]$, where a_0 is a constant and k_B denotes the Boltzmann constant. The internal energy of the gas is

(a) $\frac{3}{2}Nk_BT$ (b) $\frac{5}{2}Nk_BT$

(c) $Nk_BT\ln\left[a_0V(k_BT)^{5/2}/N\right]-\frac{3}{2}Nk_BT$ (d) $Nk_BT\ln\left[a_0V/(k_BT)^{5/2}\right]$

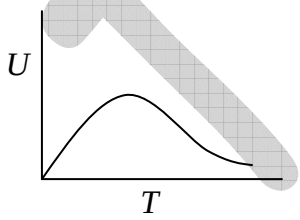
Q16. The entropy S of a thermodynamic system as a function of energy E is given by the following graph

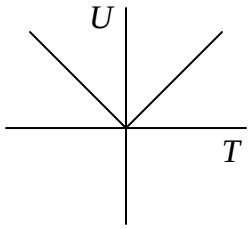


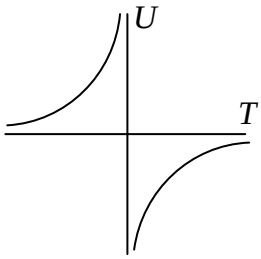
The temperatures of the phases A, B and C, denoted by T_A, T_B and T_C, respectively, satisfy the following inequalities:

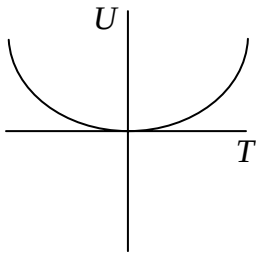
(a) $T_C > T_B > T_A$ (b) $T_A > T_C > T_B$ (c) $T_B > T_C > T_A$ (d) $T_B > T_A > T_C$

Q17. The entropy of an ideal paramagnet in a magnetic field is given approximately by $S = S_0 - cU^2$ where U is energy of the spin system and c is constant then which one is correct plot between internal energy and temperature T where $-\infty < T < \infty$

(a)


(b)


(c)


(d)


Q18. A certain system is found to have Gibbs free energy given by

$$G(p,T) = RT\ln\left(\frac{aP}{(RT)^{5/2}}\right)$$

Where a and R are constants then specific heat at constant pressure (c_p) is given by

(a) $\frac{3}{2}R$ (b) $\frac{5}{2}R$ (c) $\frac{7}{2}R$ (d) $\frac{9}{2}R$

Q19. Helmholtz free energy is given by $F = -CT^4$ where C is constant and T is temperature in Kelvin then which one is correct relation between specific heat at constant volume C_v and entropy S is given by

(a) $C_V = 2S$ (b) $C_V = 4S$ (c) $C_V = 3S$ (d) $C_v = \frac{3}{2}S$

Q20. If C_V is the specific heat of the ideal gas then which of the following is correct of Vander wall gases for same degree of freedom .

(a) $dU = C_V dT$ (b) $dU = -\frac{a}{V^2}dV$

(c) $dU = C_V dT - \frac{a}{V^2}dV$ (d) $dU = C_V dT + \frac{a}{V^2}dV$

Q21. For a Van der Waals gas the equation of the adiabatic curve in the variables T, V;

(a) $T(V-b)^{R/C_P} = cons\tan t$ (b) $T(V-b)^{R/C_V} = cons\tan t$

(c) $T(V-b)^{-R/C_P} = cons\tan t$ (d) $T(V-b)^{-R/C_V} = cons\tan t$

MSQ (Multiple Select Questions)

Q22. If H is enthalpy and G is Gibbs free energy of the thermodynamic system then which of the following is correct

(a) $H = G - TS$

(b) $H = G + TS$

(c) $H = -T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_P$

(d) $H = T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_P$

Q23. Which of the following statements are correct .

(a) The first energy equation is be given by $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

(b) The value of $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for Ideal gas

(c) The value of $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for Vander Waal's gases .

(d) The second energy equation is given by $\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P - P$

Q24. Which of following is correct for heat capacity at constant pressure C_P and volume C_V

(a) $C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$

(b) for van der waal's gas $C_p - C_V = \frac{R}{1 - 2a\left(1 - b/V\right)^2 / VRT}$

(c) van der Waal's gas behave like a ideal as high temperature

(d) for Ideal gas $c_p - c_V = R$

Q25. Which of the following is correct?

(a) $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

(b) $C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

(c) $C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2$

(d) $C_P - C_V = T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2$

Q26. If α is volume expansivity of substance and β_T is isothermal compressibility β_S is adiabatic compressibility and it is given that $C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$ then which one of the following is correct

(a) $C_P - C_V = -\frac{T\alpha^2 V}{\beta_T}$ (b) $C_P - C_V = \frac{T\alpha^2 V}{\beta_T}$

(c) $\beta_s - \beta_T = \frac{T\alpha^2 V}{C_P}$ (d) $\beta_s - \beta_T = -\frac{T\alpha^2 V}{C_P}$

Q27. Which of the following is correct if all variable have usual meaning in thermodynamics

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (b) $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$

(c) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_V$ (d) $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_V$

Q28. One mole of oxygen is expanded from a volume V_1 to V_2 at a constant temperature T. If the The gas is assumed to be a Van der Waals gas

(a) the increment of the internal energy of the gas is zero

(b) the increment of the internal energy of the gas $a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

(c) heat exchange during the process is $RT \ln \frac{V_2 - b}{V_1 - b} + a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$

(d) heat exchange during the process is $RT \ln \frac{V_2 - b}{V_1 - b}$

Q29. The free energy for a photon gas is given by $F = -\left(\frac{a}{3}\right)VT^4$, where a is a constant. The entropy S and the pressure P of the photon gas are

(a) $S = \frac{4}{3}aVT^3$ (b) , $P = \frac{a}{3}T^4$

(c) $S = -\frac{4}{3}aVT^3$ (d) $P = \frac{4a}{3}T^4$

Solutions
MCQ (Multiple Choice Questions) Solution

Ans. 1: (d)

Ans. 2: (a)

Solution: The sudden stretching of wire of compression of liquid is given by

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Ans. 3: (c)

Solution: The rate of change of temperature pressure is given by Clausius-Clapeyron equation which is given as $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$, L is latern heat

This can be derived by Maxwell's first thermodynamical relation given as

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Ans. 4: (a)

Solution: from Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_V$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = -\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P \Rightarrow \left(\frac{\partial}{\partial P}\left(\frac{T\partial S}{\partial T}\right)_P\right)_T = -T\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P$$

$$\Rightarrow \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_V \quad \text{and} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{so} \quad \left(\frac{\partial C_P}{\partial P}\right)_T = -TV\alpha^2$$

Ans. 5: (a)

Solution: $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$ from Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and

$$\left(\frac{T\partial S}{\partial T}\right)_V = C_V$$

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Ans. 6: (b)

Solution: $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial P}\right)_T dP$ from Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ and

$$\left(\frac{T\partial S}{\partial T}\right)_V = C_P$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dV$$

Ans. 7: (a)

Solution: $dF = -SdT - PdV$

Ans. 8: (d)

Solution: $dG = -SdT + VdP$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_p \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

And. 9: (a)

Solution: Heat exchange is path dependent, so it is not perfect differential.

Ans. 10: (b)

Solution: $dH = TdS + VdP \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$ and $T = \left(\frac{\partial H}{\partial S}\right)_P$

Ans. 11: (d)

Solution: The change in Gibb's free energy is given as

$$dG = VdP - SdT$$

at constant P, $dP = 0$ at constant T, $dT = 0$ $G \Rightarrow$ constant

Ans. 12: (a)

Solution: Enthalpy $H = PV + U$

From laws of thermodynamics is given as

$$TdS = dU + PdV$$

so, $G = U + PV - TS$

$\Rightarrow dG = dU + d(PV) - d(TS)$

$= dU + PdV + VdP - SdT - TdS$ by equation (i)

$dG = VdP - SdT$

$dG = VdP - S\,dT$ (ii)

for isobaric $dP = 0$, for isothermal $dT = 0$

so, equation (ii) becomes $dG = 0$

$\Rightarrow G = \text{constant}$

Ans. 12: (d)

Ans. 13: (a)

Solution: Gibb's function is given as

$G = H - TS$ And The enthalpy $H = U + PV$

$G = U + PV - TS \Rightarrow dG = dU + d(PV) - d(TS)$

$dG = dU + PdV + VdP - TdS - SdT$

$dG = VdP - SdT$

According to question the process is isobaric i.e., $SdP = 0$ isothermal i.e., $dT = 0$. So Equation (v) becomes as $dG = 0 \Rightarrow G = c$

Ans. 14: (b)

Solution: $TdS = dE + PdV \Rightarrow dE = TdS - PdV \Rightarrow \left(\frac{\partial E}{\partial S}\right)_V = T \Rightarrow T = \frac{3bS^2}{VN}$

Ans. 15: (b)

Solution: $F = -Nk_BT \ln\left[a_0 V (k_BT)^{5/2} / N\right]$, $F = U - TS$, $U = F + TS$

$dF = -SdT - PdV \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S$ or $S = -\left(\frac{\partial F}{\partial T}\right)_V \Rightarrow U = F - T\left(\frac{\partial F}{\partial T}\right)_V$

$F = -Nk_BT \ln\left(CT^{5/2}\right)$ where $C = \frac{a_0 V k_B^{5/2}}{N}$

$\left(\frac{\partial F}{\partial T}\right)_V = -Nk_B \ln\left(CT^{5/2}\right) - Nk_BT \frac{C}{CT^{5/2}} \frac{5}{2} T^{3/2} \Rightarrow T\left(\frac{\partial F}{\partial T}\right)_V = -Nk_BT \ln\left(CT^{5/2}\right) - \frac{5}{2} Nk_BT$

$$T\left(\frac{\partial F}{\partial T}\right)_V = F + \frac{5}{2}Nk_BT \Rightarrow U = F - T\left(\frac{\partial F}{\partial T}\right)_V = \frac{5}{2}Nk_BT\ .$$

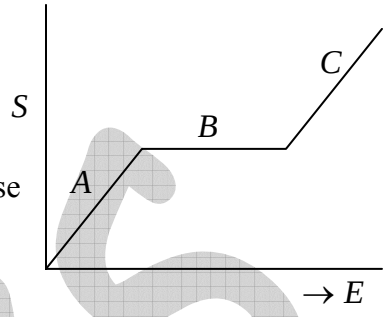
Ans. 16: (c)

Solution: Now temperature of phase TA, TB, TC

Now $\left(\frac{dS}{dE}\right) = \frac{1}{T}$

Now $\frac{dS}{dE}$ will be stops then it will be zero for B - phase

So $T_B = \infty$



And in C and A phases external energy of C phase is more so $T_C > T_A$

Now $T_B > T_C > T_A$

Ans. 17: (c)

Solution: $\mathrm{T} = \left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = -\frac{1}{2\mathrm{cU}}$ i.e $\mathrm{U} = -\frac{1}{2\mathrm{cT}}$

Ans. 18: (b)

Solution: $\mathrm{S} = -\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \frac{5}{2}\mathrm{R} - \mathrm{R}\ln\left[\frac{\mathrm{ap}}{(\mathrm{RT})^{5/2}}\right]$

$$\mathrm{C_p} = \mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right) = \frac{5}{2}\mathrm{R}$$

Ans. 19: (c)

Solution: $S = -\left(\frac{\partial F}{\partial T}\right)_V = 4CT^3$

$$\mathrm{TdS} = \mathrm{C_V dT} + \mathrm{PdV} \Rightarrow dS = \frac{C_V}{T}dT + \frac{P}{C_V}dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow C_V = 3S$$

Ans. 20: (d)

Solution: $U = U(T,V) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \Rightarrow dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \quad \text{so} \quad dU = C_V dT + \frac{a}{V^2} dV$$

Ans. 21: (b)

Solution: $\left(P + \frac{a}{V^2}\right)(V-b) = RT$ and $dU = C_V dT + \frac{a}{V^2} dV$

For adiabatic process: $dQ = 0 = dU + pdV$

$$-C_V dT - \frac{a}{V^2} dV = \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) dV$$

$$-C_V dT = dV\left[\frac{RT}{V-b}\right]$$

$$-\int \frac{C_V dT}{RT} = \int \frac{dV}{V-b}$$

$$-\frac{C_V}{R} \ln Tk = \ln(V-b)$$

$$V - b = (Tk)^{-C_V/R}$$

$$V - b = T^{-C_V/R} \times k^{-C_V/R}$$

$$(V-b)T^{C_V/R} = k^{-C_V/R}$$

$$T(V-b)^{R/C_V} = cons\tan t$$

MSQ (Multiple Select Questions)

Ans. 22: (b) and (c)

Solution: $dG = -SdT + VdP \Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S$

$$G = H - TS \qquad H = G + TS \quad \text{so } H = G - T\left(\frac{\partial G}{\partial T}\right)_P \quad \Rightarrow H = -T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_P$$

Ans. 23: (a), (b) and (c)

Solution: The first law of thermodynamics is given as

$$dU + PdV = TdS$$

$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$ From Maxwell's second relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

For real gas $PV = nRT$ so $\left(\frac{\partial U}{\partial V}\right)_T = 0$

For Vander wall's $\left(P - \frac{a}{V^2}\right)(V-b) = nRT$ so $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Ans. 24: (a), (b), (c) and (d)

Solution: (a) From $H = U + PV$, we obtain,

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

Let $U = U\left[T, V(T,P)\right]$.

Let $U = U\left[T, V(T,P)\right]$. The above expression becomes

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

Hence $$c_P - c_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

(b) to find $c_p - c_v$ for a Van der Waals gas $\left(P + \frac{a}{V^2}\right)(V-b) = RT$

For the Van der Waals gas, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left[\frac{RT}{V-b} - \frac{2a(V-b)}{V^3}\right]}$$

Hence, $c_p - c_v = \dfrac{R}{1-2a\left(1-b/V\right)^2/VRT}$

(c) and d) When $V \,\&\, T \to \infty, c_P - c_V \to R$, which is just the result for an ideal gas.

Ans. 25: (a) and (c)

Solution: $S = S(T,V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \Rightarrow T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$P = P(T,V)$

$dP = \left(\dfrac{\partial P}{\partial T}\right)_V dT + \left(\dfrac{\partial P}{\partial V}\right)_T dV$ for constant pressure $dP = 0$

Put $\left(\dfrac{\partial P}{\partial T}\right)_V = -\left(\dfrac{\partial P}{\partial V}\right)_T \left(\dfrac{\partial V}{\partial T}\right)_P$ in $C_P - C_V = T\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P$ one will

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)^2_P$$

Ans. 26: (b) and (d)

Solution: $C_P - C_V = -T\left(\dfrac{\partial P}{\partial V}\right)_T \left(\dfrac{\partial V}{\partial T}\right)^2_P$ it is known $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ and $\beta_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T$

So $C_P - C_V = \dfrac{T\alpha^2 V}{\beta_T}$,we know that $\dfrac{C_P}{C_V} = \dfrac{\beta_T}{\beta_S} = \gamma$

$$\gamma - 1 = \frac{T\alpha^2 V}{C_V \beta_T} \Rightarrow \beta_s - \beta_T = \frac{\beta_S}{\beta_T}\frac{T\alpha^2 V}{C_V} \quad \Rightarrow \beta_s - \beta_T = -\frac{T\alpha^2 V}{C_P}$$

Ans. 27: (a), (b) and (d)

Solution: from Maxwell relation $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right)_V \Rightarrow \left(\frac{\partial}{\partial V}\left(\frac{T\partial S}{\partial T}\right)_V\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right)_V$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Similarly another Maxwell relation is given by $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_V$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = -\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P \Rightarrow \left(\frac{\partial}{\partial P}\left(\frac{T\partial S}{\partial T}\right)_P\right)_T = -T\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P$$

$$\Rightarrow \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_V$$

Ans. 28: (b) and (d)

Solution: (a) for Vander waal's gas $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

$$\Delta U = \frac{a}{V_1} - \frac{a}{V_2} = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

(b) We know

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$P = \frac{RT}{V-b} - \frac{a}{V^2}$ and work done $W = \int_{V_1}^{V_2} PdV$

$$\Delta W = dW = \int_{V_1}^{V_2} \frac{RT}{V-b}dV - \int_{V_1}^{V_2} \frac{a}{V^2}dV = RT\ln\frac{V_2 - b}{V_1 - b} + a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

Now $\Delta Q = \Delta W + \Delta U = RT\ln\frac{V_2 - b}{V_1 - b} + a\left[\frac{1}{V_2} - \frac{1}{V_1}\right] + a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$ $\Delta Q = RT\ln\frac{V_2 - b}{V_1 - b}$

Ans. 29: (a) and (b)

Solution: $dF = -SdT - PdV$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad , \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

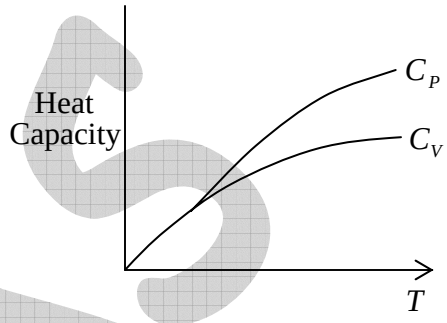
Chapter - 6

Phase Transition and Low Temperature Physics

6.1 Third Law of Thermodynamics and Attainable of Low Temperature

The third law of thermodynamics is some time stated as follows:

It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its zero point value in a finite number of operations.



Properties of material at low temperature

At $T \to 0$

$$C_P = C_V = 0$$

At $T \to 0$

$$S \to 0$$

At $T \to 0$

Thermal expansion coefficient $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = 0$

$$\alpha = 0$$

6.2 Production of Low Temperature: The Joule – Kelvin Expansion:

The Joule – Kelvin Expansion is essentially a continuous steady – state flow process in which a compressed gas is made to expand adiabatically irreversibly through a porous plug and do work.

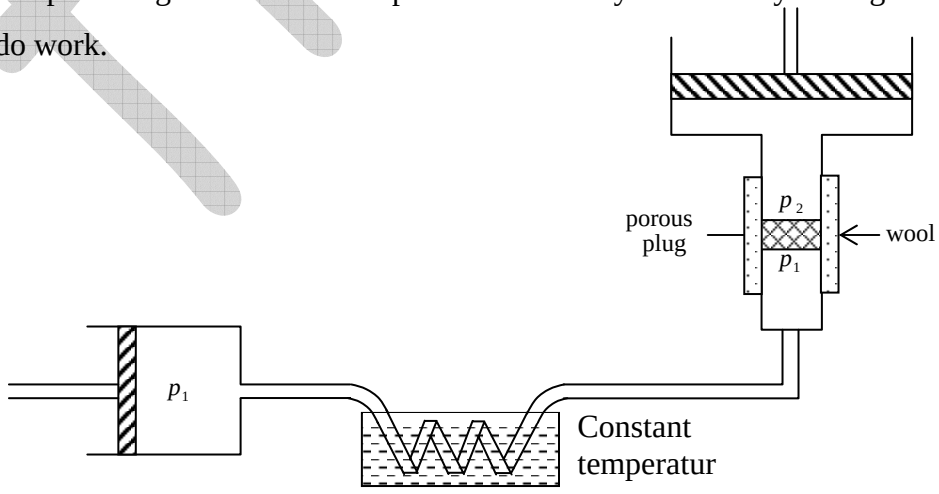


Fig: A schematic diagram of the porous-plug experiment for Joule-Kelvin

Let us assume that we start off with a gas of internal energy U_1 and volume V_1. After passing through the porous plug let find internal energy and volume of the gas by U_2 and V_2. No heat enters the system.

So this work has to performed at the expense of internal energy

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

$$H_1 = H_2$$

Joule – Kelvin expansion is isenthalpic process

$$H = H(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)dP$$

Hence H does not change $dH = 0$

The μ is defined $\left(\frac{\partial H}{\partial P}\right)_H$

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu = \frac{1}{C_P}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right) = \frac{T^2}{C_P}\left(\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P\right)$$

where μ is known as the Joule – Kelvin Coefficient.

The equation defines a curve in the (T, P) plane and is known as the inversion curve when μ = 0.

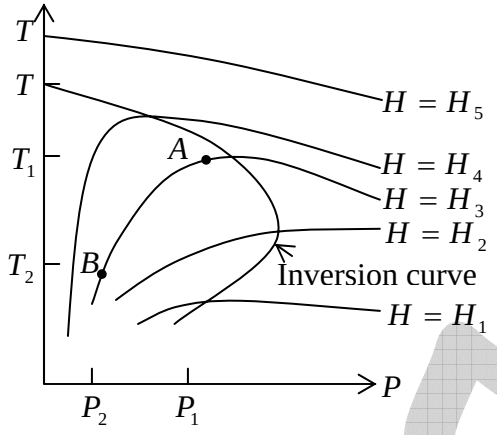


Figure: Curves of constant enthalpy. The bold curve is the inversion curve. Inside it, the gas is cooled on expansion. The temperature change $\Delta T = T_2 - T_1$ produced in a

A series of isoenthalphs, i.e. curve with $H(T,P)$ = constant.

At $T = T_j$ $\mu = 0$ known as inversion temperature.

$T < T_i$ and $\mu =$ Positive. There is heating effect of gases i.e. temperature and pressure move in same direction.

$T > T_i$ $\mu =$ Negative. There is cooling effect i.e. temperature and pressure move in opposite direction.

Example: (a) For van der Waals gas. Prove that inversion temperature $T_i = \dfrac{2a}{Rb}$ where a and b are parameter used in van der Waals gas.

(b) Why Hydrogen and helium shows heating effect as pressure increased at constant enthalphy.

Solution: (a) $$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right)$$

For van der Waals gas

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P + \frac{a}{V^2}\right)} - \frac{2a}{V^3}(V-b)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{(V-b)}{T\left(1-\frac{2a(V-b)^2}{RTV^3}\right)}$$

since $b << V$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}\left(1-\frac{b}{V}\right)\left(1-\frac{2a}{RTV}\right)^{-1} = \frac{V}{T}\left(1-\frac{b}{V}\right)\left(1+\frac{2a}{RTV}\right)$$

$$= \frac{V}{T}\left(1-\frac{b}{V}+\frac{2a}{RTV}\right). \qquad T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b$$

$$\mu = \frac{1}{C_p}\left(\frac{2a}{RT}-b\right)$$

For inversion temperature

$$\mu = 0 \quad \Rightarrow \qquad \frac{2a}{RT_i} = b \qquad T_i = \frac{2a}{Rb}$$

(b) Since inversion temperature of Hydrogen and Helium is very small. For cooling effect initial temperature must be smaller than inversion temperature, but for Helium and Hydrogen inversion temperature is very small

so it is not possible to achieve initial condition lower than inversion temperature so Helium and Hydrogen give heated effect.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right) \qquad dT = \frac{1}{C}T\left(\frac{\partial V}{\partial T}\right)_P dP - VdP$$

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T} = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P dP = -\left(\frac{\partial P}{\partial T}\right)_V dV$$

6.3 Phase Transition

A phase of a thermodynamic system and the state of matter has uniform physical properties.

A phase transition is the transformation of thermodynamic system from one phase or state of matter to another.

During a phase transition of a given medium certain properties of the medium change, often discontinuously, as a result of some external condition, such as temperature, pressure and others.

Gibbs phase rule: It is proposed by Josiah Willard Gibbs, which is given by

$$F = C - P + 2$$

Where C is number of components, P is the number of phase in thermodynamic equilibrium with each other and F is number of degree of freedom.

Phase: A phase is form of matter that is homogeneous in chemical composition and physical state.

Typical phases are solid, liquid and gas. Two immiscible (or liquid mixture with different compositions) separated by distinct boundary are countered as two different phase.

Components: The number of components is the number of chemically independent constituents of the system, i.e. minimum number of independent species necessary to define the composition of all phase of the system.

The number of degree of freedom (F) in the context is the number of intensive variable which are independent to each other.

6.3.1 First Order Phase Transition

Let us consider one component system in which system having only one kind of constituent particles . for first order phase transition $P-T$ diagram are shown in fig 1 . Depending on the system, at some values for temperature and pressure, the three phases of the system may be found in equilibrium. In the P-T diagram, the line OA represents equilibrium between solid and liquid phases, the line OB represents equilibrium between solid and gas phases, and the line OC represents equilibrium between liquid and gas phases. The point O where all the three phases are in equilibrium, is known as a **triple**

point. The line OC terminates at the point C, called the **critical point**. Beyond this point, the gas phase cannot be converted into the liquid phase. In figure 1, the point C is at the apex of the *P*-*V* curve at the critical temperature T_c. For the temperature $T > T_c$, the gas phase of the matter cannot be converted into the liquid phase, but for $T < T_c$, the gas phase can in general be converted into the liquid phase.

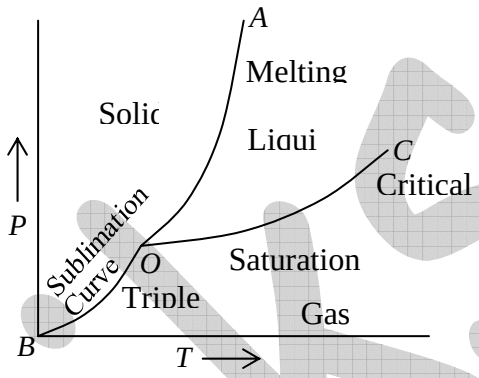


Figure 1: P-T phase of one component

6.3.2 Equilibrium Between Two Phases

Let us consider an isolated system having a matter which is existing in two phases, denoted by 1 and 2, simultaneously in equilibrium with each other (Figure 2). Suppose V_1 and V_2 are volumes, N_1 and N_2 the number of particles, E_1 and E_2 the internal energies, and S_1 and S_2 the entropies of the two phases, respectively. For each phase, entropy is a function of its volume, number of particles (mass) and internal energy.

From these relations, it follows that

$T_1 = T_2$ thermal equilibrium

$P_1 = P_2$ mechanical equilibrium

$\mu_1 = \mu_2$ chemical equilibrium

Hence, when two different phases of the matter are in equilibrium, their temperatures, pressures and chemical potentials must be equal. If the chemical potentials are expressed as functions of pressure and temperature, we have

$$\mu_1(P,T) = \mu_2(P,T)$$

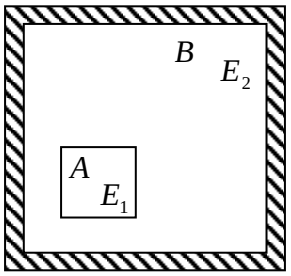


Figure 2: Equilibrium of two phases of an isolated one component system

where P (= P_1 = P_2) and T (= T_1 = T_2) are the common pressure and temperature, respectively, of the two phases in equilibrium. Thus, from above equation , we have

$$G_1(P,T)N_1 = G_2(P,T)N_2$$

$$\frac{G_1}{N_1} = \frac{G_2}{N_2}$$

where $G_1(P, T)$ and $G_2(P, T)$ are the Gibbs free energies, and N_1 and N_2 the number of particles in the two phases, respectively. Since during the phase transition, the number of particles is not changing (i.e., $N_1 = N_2$), we have

$$G_1(P,T) = G_2(P,T)$$

Hence, during the phase transition, the Gibbs free energy does not change. Gibbs energies G_1 and G_2 of the two phases 1 and 2, respectively, can be exhibited as shown in figure 4.

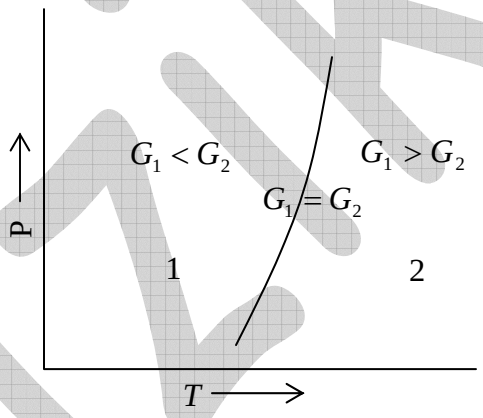


Figure 3: Phase equilibrium curve ($G_1 - G_2$) separating two phases 1 and 2.

6.3.3 Clapeyron-Clausius equation

When the two phases, denoted by 1 and 2, of the given matter are in equilibrium, we have

$$G_1(P,T) = G_2(P,T)$$

where G_1 and G_2 are Gibbs free energies of the two phases, respectively, and P (= P_1 = P_2) and T (= T_1 = T_2) are the common pressure and temperature, respectively, of the two phases. In the P-T diagram, along the phase-transition line, let us consider a point, where the pressure is P + dP and the temperature is $T + dT$ so that we have

$$G_1(P + dP, T + dT) = G_2(P + dP, T + dT)$$

Using Taylor series expansion and neglecting the higher order terms, we have

$$G_1(P,T)+\left(\frac{\partial G_1}{\partial P}\right)_T dP+\left(\frac{\partial G_1}{\partial T}\right)_P dT = G_2(P,T)+\left(\frac{\partial G_2}{\partial P}\right)_T dP+\left(\frac{\partial G_2}{\partial T}\right)_P dT$$

Using above two equation we get

$$V_1 dP - V_2 dP - S_1 dT + S_2 dT = 0$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{L}{T}$$

where $\Delta H(= H_2 - H_1)$ is the change in heat (enthalpy) which is the molar latent heat L. thus, from equation an we have

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

for $V_2 > V_1$, we have

$$\left(\frac{\partial G_2}{\partial P}\right)_T \rangle \left(\frac{\partial G_1}{\partial P}\right)_T \qquad \text{(A)}$$

further, for $S_2 > S_1$, we have

$$\left(\frac{\partial G_2}{\partial T}\right)_P \rangle \left(\frac{\partial G_1}{\partial T}\right)_P \qquad \text{(B)}$$

6.3.4 Liquid-Vapour Phase Transition

Let us consider a phase transition from a liquid state to a vapor one. If V_i and V_g, respectively, denote the volume in the liquid and gas phases, and L_v is the heat of vaporization (latent heat for the transition from liquid to vapour), the Clapeyro-Clausius equation is

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_i)}$$

Since in the phase transition, V_g is always greater than V_i and the heat of vaporization L_v is positive and we have

$$\frac{dP}{dT} > 0$$

It shows that the boiling point of a liquid increases with the increase in pressure.

Now, if the vapour pressure is low, i.e., $V_g >> V_i$, in comparison to V_g, and we have

$$\frac{dP}{dT} = \frac{L_v}{TV_g}$$

Using the ideal gas equation, $PV_g = RT$, we have

$$\frac{dP}{dT} = \frac{L_v P}{RT^2} \qquad \frac{dP}{P} = \frac{L_v}{R}\frac{dT}{T^2}$$

$$\ln[P(T)] = -\frac{L_v}{R}\frac{1}{T} + C$$

where C is a constant of integration. At the critical point, we have $P = P_c$, $T = T_c$ and equation is

$$\ln[P_c(T_c)] = -\frac{L_v}{R}\frac{1}{T} + C$$

$$P(T) = P_c(T_c)\exp\left[\frac{L_v}{R}\left(\frac{1}{T_c} - \frac{1}{T}\right)\right]$$

Here, we have assumed that the heat of vapourisation L_v is independent of the temperature. However, it depends on the temperature. Suppose it varies as $L_v = a - bT$, then for an ideal gas at low pressure, we have

$$\frac{dP}{P} = \frac{(a - bT)}{R}\frac{dT}{T^2}$$

$$\ln[P(T)] = -\frac{a}{R}\frac{1}{T} - \frac{b}{R}\ln(T) + C$$

where C is a constant of integration. At the critical point, we have $P = P_c, T = T_c$ and equation is

$$\ln[P_c(T_c)] = -\frac{a}{R}\frac{1}{T_c} - \frac{b}{R}\ln(T_c) + C$$

On subtracting equation from and rearranging, we have

$$\ln\left[\frac{P(T)}{P_c(T_c)}\right] = \frac{a}{R}\left(\frac{1}{T_c} - \frac{1}{T}\right) + \frac{b}{R}\ln\left(\frac{T_c}{T}\right)$$

6.3.5 Properties of First Order Phase Transition

(1) Gibbs free energy is continuous

(2) First order derivative with respect to temperature and pressure have finite discontinuity i.e. entropy (S) and pressures (P) have finite discontinuity.

(3) Second and more higher order differential is infinite

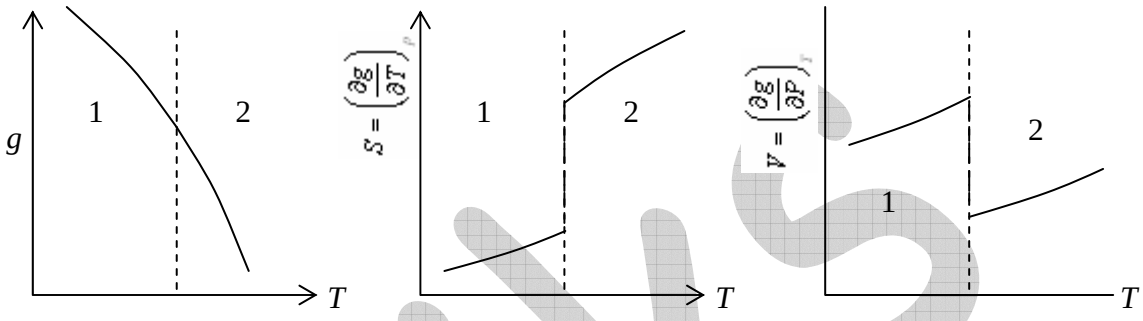


Fig. 4: A schematic representation of first order phase transitions

Example: For a two phase system in equilibrium, p is a function of T only, so that

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_S$$

Show that

$$\frac{C_V}{\beta_S} = TV\left(\frac{dP}{dT}\right)^2$$

Solution: Let us take T and V as independent variables and write

$$S = S(T,V)$$

so that

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

For an adiabatic process, it yields

$$\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_S$$

Using first Maxwell relation, we obtain

$$\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S$$

Since $C_V = T\left(\frac{\partial P}{\partial T}\right)_V$ we can write

$$C_V = -T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S \qquad = -T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_S \left(\frac{\partial P}{\partial T}\right)_S$$

$$= TV\beta_S \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_S \qquad = TV\beta_S \left(\frac{dP}{dT}\right)^2$$

where β_S is adiabatic compressibility.

Example: Calculate under what Pressure water would boil at 120° C. One gram of steam occupies a volume of 1677 cm^3. Latent heat of steam = 540 cal/g, J = 4.2×10^7 erg/cal. atmospheric pressure = 1.0×10^6 dyne/cm^3

Solution: $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$ $\qquad dP = \frac{L \times dT}{(V_2 - V_1)}$

$V_2 = 1677\ cm^3/g$ $\qquad V_2 = 1\ cm^3/g$

$L = 4.2 \times 10^7 \times 540$ erg/g $\qquad dT = 20^\circ$ k

$dP = 0.725$ $\qquad P_2 - P_1 = .725$

$P_2 = 0.725 + P_1 = 1 + 0.725 = 1.725$

Example: Liquid helium – 4 has normal boiling point of 4.2 k. However at pressure at 1 mm of mercury it boils at 1.2 k. Estimate the average latent heat of vaporization of helium in this temperature range.

Solution: $\frac{dP}{dT} = \frac{L}{T(V_g - V_e)} = \frac{L}{TV_g}$

$PV_g = RT$ $\qquad V_g = \frac{RT}{P}$

$$\frac{dP}{dT} = \frac{L}{T\frac{RT}{P}} \qquad \frac{dP}{dT} = \frac{LP}{RT^2}$$

$$\int_{P_0}^{P} \frac{dP}{P} = \frac{L}{R}\int_{T_0}^{T} \frac{dT}{T^2} \qquad \ln\frac{P}{P_0} = \frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$L = \frac{R\ln\frac{P}{P_0}}{\frac{1}{T_0} - \frac{1}{T}}$$

P_0 = 746 mm $\qquad$ T_0 = 4.2 k

P_1 = 1 mm $\qquad$ T = 1.2

L = 93 J/mol.

Example: Liquid helium boils at temperature T_0 when its vapour pressure is equal to P_0 we now pump on the vapour and reduce the pressure to much smaller value P. Assume that the Latent heat L is approximately independent at temperature and helium vapour density is much smaller than that of liquid, calculate the approximate temperature T_m of the liquid in equilibrium with its vapour at pressure P.

Express your answer in terms of L, T_0, P_0, P_m and any other required constants.

Solution: $\frac{dP}{dT} = \frac{L}{T\Delta V}$ $\qquad$ $\Delta V = V_{gas} - V_{liq} \approx V_{gas}$

$$\frac{dP}{dT} = \frac{LP}{RT^2} \qquad \int_{P_0}^{P_m} \frac{dP}{P} = \frac{L}{R}\int_{T_0}^{T_m} \frac{dT}{T^2}$$

$$T_m = \frac{T_0}{1 + \frac{RT_0}{L}\ln\frac{P_0}{P_m}}$$

Example: In the phase transition from a liquid state to a vapour state. The heat of vapourisation L_v varies with temperature T as $L_v = a - bT^{1/2}$. Considering the gas as an ideal one at low pressure, show that the pressure $P(T)$ at temperature T in terms of the critical pressure $P_c(T_c)$ at critical temperature T_c is given by

$$\ln\left[\frac{P(T)}{P_c(T_c)}\right] = \frac{a}{R}\left(\frac{1}{T_c} - \frac{1}{T}\right) + 2\frac{b}{R}\left(\frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}}\right)$$

Solution: Clapeyron-Clausius equation for the phase transition from liquid to vapour is

$$\frac{dP}{dT} = \frac{L_v}{T(V_g - V_i)}$$

where L_v is the heat of vapourisation and V_i and V_g, respectively, denote the volume is the liquid and gas phase. For low pressure, $V_g >> V_i$

$$\frac{dP}{dT} = \frac{L_v}{TV_g}$$

Using $L_v = a - bT^{1/2}$, we have

$$\frac{dP}{dT} = \frac{a - bT^{1/2}}{TV_g}$$

For an ideal gas equation, $PV_g = RT$, and thus,

$$\frac{dP}{dT} = \frac{\left(a - bT^{1/2}\right)P}{RT^2}$$

$$\frac{dP}{dT} = \frac{\left(a - bT^{1/2}\right)P}{RT^2}dT = \frac{a}{R}\frac{dT}{T^2} - \frac{b}{R}\frac{dT}{T^{3/2}}$$

$$\ln[P(T)] = -\frac{a}{R}\frac{1}{T} + \frac{b}{R}\frac{1}{T^{1/2}} + C$$

On subtracting equation above and rearranging, we have

$$\ln\left[\frac{P(T)}{P_c(T_c)}\right] = \frac{a}{R}\left(\frac{1}{T_c} - \frac{1}{T}\right) + \frac{2b}{R}\left(\frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}}\right)$$

Derive Glausius-Clapeyron equation from Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\delta Q = L dm$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{V_{vap} - V_{liq}} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T\left(V_{vap} - V_{liq}\right)}$$

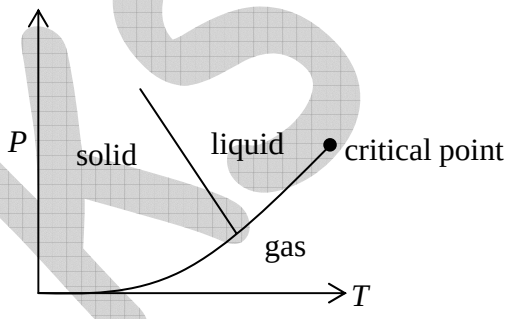
(b) Draw Phase diagram for water and explain why water expand after freezing.

Phase diagram for water

The slope of solid liquid phase is negative.

So from Clausius:-

Clapeyron equation



$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{L}{T\left(V_{liq} - V_{solid}\right)}$$

$$\left(\frac{\partial P}{\partial T}\right) = -ve \qquad V_{liq} - V_{solid} < 0 \qquad V_{liq} < V_{solid}$$

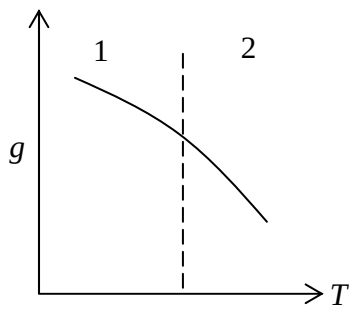
so water expand on freezing

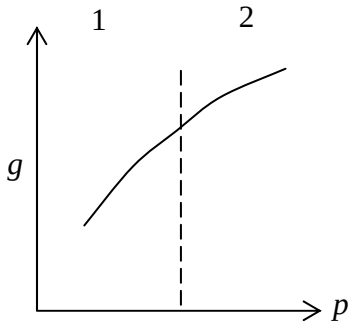
6.3.6 Second Order Phase Transition:

In some cases the state of matter does not change but the arrangement of its constituent particle changes. This kind of phase transition is known as second order phase transition.

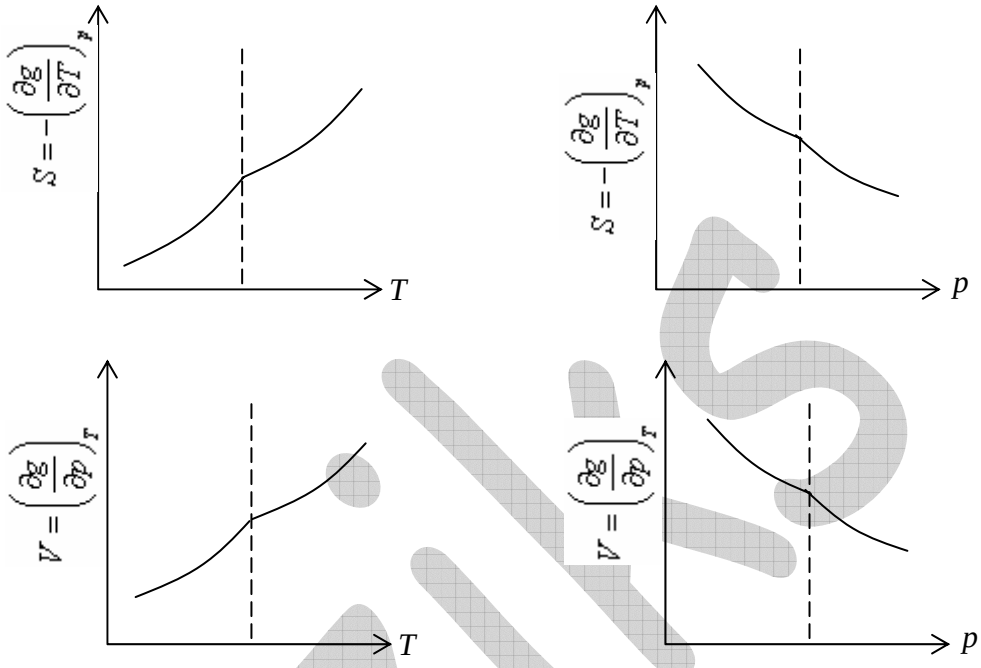
In the case of second order phase transition, no heat is evolved or absorbed. In second order phase transition

1. Gibbs free energy is continuous





2. First order differential of Gibbs energy with respect to temperature ie entropy are changes smoothly



3. Second order differential of Gibbs energy with respect to temperature ie specific heat and second order differential of Gibbs energy with respect to pressure ie isothermal and isobaric expansivity have finite discontinuity at critical temperature.

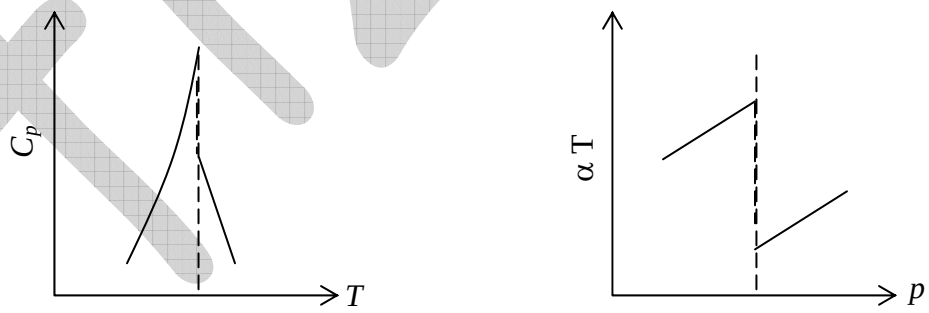


Figure 5: A schematic representation of a second order phase transition

4. The thermodynamic property which are determine by more than second order derivative will be infinite at critical temperature,

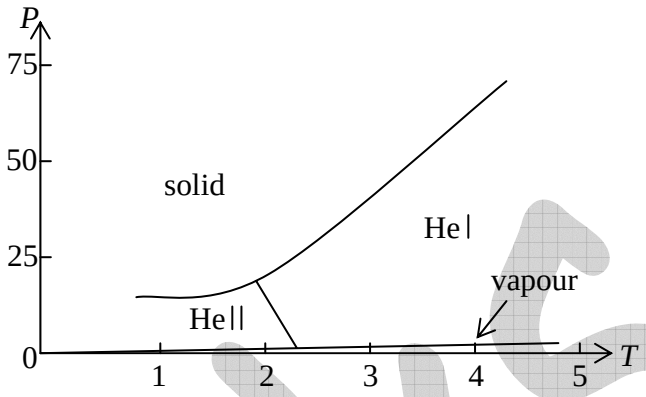


Figure: Phase diagram of helium

MCQ (Multiple Choice Questions)

Q1. In phase transition of first order, there is a finitely discontinuity at the transition point of

(a) Gibbs free energy G

(b) The first-order derivatives of G

(c) The second -order-derivatives of G

(d) The higher -order-derivatives more than second order of G

(where G is the Gibbs function)

Q2. In phase transition of second order, there is a infinitely discontinuity at the transition point of G is the Gibbs function

(a) Gibbs free energy G

(b) The first-order derivatives of G

(c) The second -order-derivatives of G

(d) The higher -order-derivatives more than second order of G

(where G is the Gibbs function)

Q3. Which of the following is finitely discontinuous at transition temperature for first order transition?

(a) Gibbs free energy (b) Entropy

(c) Specific Heat (d) Volume expansibility

Q4. The Clausius-Clapeyron equation indicates that the increase of pressure increases the melting point:

(a) in the case of all substances

(b) in the case of substances which expand on solidification

(c) in the case of substances which contract on solidification

(d) in the case of substances which neither expand nor contract on solidification

Q5. Consider the following statements in respect of first-order phase transition:

1. Clausius-Clapeyron latent heat equation holds well in the first-order phase transition.

2. There is change in entropy and volume in the first-order phase transition.

Which of the above statements is/are correct?

(a) 1 only (b) 2 only (c) Both 1 and 2 (d) Neither 1 nor 2

Q6. The Joule-Thomson expansion produced cooling:

(a) at all initial temperatures and pressures

(b) above certain initial temperature

(c) above certain initial pressure

(d) below certain initial temperature

Q7. After Joule-Thomson expansion, the gas is:

(a) always heated

(b) heated or cooled depending upon the initial temperature of the gas

(c) neither heated nor cooled at any temperature

(d) always cooled

Q8. Match List I and List II and select the correct answer using the codes given below the Lists:

List I	**List II**
A. Temperature of inversion in Joule-Thomson effect is related to	1. $\left(\frac{\partial U}{\partial V}\right)_T = 0$
B. For perfect gases	2. $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$
C. For a perfect gas Joule-Thomson effect vanishes because	3. $\frac{\partial}{\partial P}(PV)_T \neq 0$
D. Deviation from Boyle's law implies	4. $\left(T\frac{\partial V}{\partial T} - V\right) = 0$

Codes:

	A	B	C	D
(a)	2	4	1	3
(b)	3	1	4	2
(c)	2	1	4	3
(d)	3	4	1	2

Q9. On the inversion curve, the Joule-Thomson coefficient is:

(a) positive (b) zero (c) negative (d) infinite

MSQ (Multiple Select Questions)

Q10. Which of the following is correct statement about first order phase transition.

(a) The Gibbs free energy is continuous at transition temperature

(b) The entropy is finitely discontinues at transition temperature

(c) Pressure is infinitely discontinues at transition temperature

(d) Specific heat is infinitely discontinuous at transition temperature

Q11. Which of the following is incorrect statement about second order phase transition?

(a) The Gibbs free energy is continuous at transition temperature

(b) The entropy is finitely discontinues at transition temperature

(c) Pressure is infinitely discontinues at transition temperature

(d) Specific heat is infinitely discontinuous at transition temperature

Q12. Which of the following is finitely discontinuous at transition temperature for second order transition?

(a) Gibbs free energy (b) Entropy

(c) Specific Heat (d) Volume expansibility

Q13. Which of the following is correct statement for phase transition?

(a) Clausius-Clapeyron latent heat equation holds well in the first-order phase transition.

(b) There is not change in entropy and volume at critical temperature in the second-order phase transition.

(c) The change of phase when water transformed in Ice is first order transition

(d) The concept of superconductor and super fluid can be explain by second order transition

Q14. Which is correctly matched for van der Waal's gas?

(a) Inversion temperature is given by $T_{\text{inversion}} = \frac{2a}{Rb}$

(b) Boyle temperature is given by $T_{\text{Boyle}} = \frac{2a}{Rb}$

(c) Critical temperature is given by $T_{\text{critical}} = \frac{8a}{27bR}$

(d) Boyle temperature is given $T_{\text{Boyle}} = \frac{a}{Rb}$

Q15. Which of the following pairs are correctly matched?

(a) Law of liquefaction of gases $\rightarrow$ triple point

(b) Law of liquefaction of gases $\rightarrow$ critical temperature

(c) Cooling effect of gas $\rightarrow$ inversion temperature

(d) Phase transition $\rightarrow$ Boyle temperature

Q16. The Joule-Thomson coefficient $\mu = \left(\frac{\partial T}{\partial P}\right)_H$:

(a) less than zero at all temperatures and pressures for ideal gas

(b) zero at all temperatures and pressures for ideal gas

(c) less than zero at all temperatures and pressures for real gas

(d) can have any value depending on pressure and temperature for real gases

Q17. Consider the following statements:

A gas can be liquefied by increasing the pressure

(a) Above the critical below critical temperature only.

(b) Only when the temperature of the enclosed gas in below the critical temperature.

(c) Only when the volume of the enclosed gas is below the critical volume.

(d) Ideal gas can not be liquefied.

Q18. Consider the following statements:

When a compressed real gas is allowed to pass through a narrow hole, the temperature

(a) Falls for some gases if $T < T_i$

(b) Falls for some gases if $T > T_i$.

(c) Rise for some gases if $T > T_i$.

(d) Rise for some gases $T < T_i$

Solutions

MCQ (Multiple Choice Questions)

Ans. 1: (b)

Solution: In first order phase transition Entropy $S=-\left(\frac{\partial G}{\partial T}\right)_P$ is discontinuous at transition point

Phase transition and low temperature physics.

Ans. 2: (d)

Ans. 3: (b)

Solution: for first order phase transition G is continuous $S=-\left(\frac{\partial G}{\partial T}\right)_P$ and $V=-\left(\frac{\partial G}{\partial p}\right)_S$ is finitely discontinuous and $C_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ is infinitely discontinuous

Ans. 4: (c)

Solution: Clausius-Clapeyron equation is given as

$$\frac{dP}{dT}=\frac{L}{T\left(V_2-V_1\right)}\Rightarrow \text{ If } V_2>V_1, \frac{dP}{dT} \text{ is positive}$$

If volume increases the pressure increases with T.

Ans. 5: (c)

Ans. 6: (d)

Solution: Cooling effect is produced when temperature is below a temperature known as temperature of inversion.

Ans. 7: (b)

Solution: The drop of temperature dT in Joule.

Thomson effect is given as

$$dT=\frac{P}{C_P M}\left(\frac{2a}{RT}-b\right) \qquad \text{(i)}$$

$\Rightarrow$ No change in temperature if $\frac{2a}{RT}-b=0\Rightarrow T_i=\frac{2a}{Rb}$

This temperature is known as temperature of inversion Equation (i)

$$\Rightarrow \quad dT > 0 \text{ if } \frac{2a}{RT} - b > 0 \quad \Rightarrow \quad T < \frac{2a}{Rb}$$

$\Rightarrow$ If temperature T of the gas is less than temperature of inversion then cooling effect is observed otherwise heating effect.

Ans. 8 : (c)

Solution: (i) The temperature of inversion in Joule-Thomson effect is the temperature above of which all gases show heating effect. Below of this all gases show colling effect and at the temperature of inversion no effect. This is given as

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$$

(ii) The internal energy of a perfect gas does not depend on volume this depends only on temperature. Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$$

For real gases $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

(iii) For a perfect gas Joule-Thomson effect vanishes because

$$\left(T\frac{\partial V}{\partial T} - V\right) = 0$$

(iv) The pressure P and PV is related as

$$PV = A + BP + CP^2 + DP^3 + \cdots$$

$A > B > C > D \ldots$ are virial constants.

The Boyle's law is applied when P is very low hence when

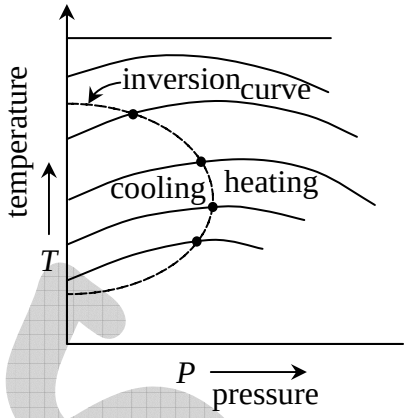
$$PV = A$$

$$\Rightarrow \frac{\partial}{\partial P}(PV) = 0$$

So, deviation from Boyle's law $\Rightarrow \quad \frac{\partial}{\partial P}(PV)_T \neq 0$

Ans. 9: (b)

Solution: An isenthalpic curve is the locus of all points representing equilibrium of same enthalpy.



If temperature is not very high then such curves pass through a maximum, called the inversion point. The locus of all inversion points is called the inversion curve. Since, towards the left of the maximum of either curve of constant enthalpy, the gas shows cooling effect, the region inside the inversion curve is the cooling region, for this region gas shows cooling effect.

On the other hand, the region outside the inversion curve the gases show heating effect and region is called region of heating.

The Joule-Thomson coefficient is defined as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

On the inversion $\mu = 0$

Thus, Joule-Thomson coefficient is zero.

MSQ (Multiple Select Questions)

Ans. 10: (a), (b) and (d)

Solution: For first order phase transition G is continuous $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = -\left(\frac{\partial G}{\partial p}\right)_S$ is finitely discontinuous and $C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ is infinitely discontinuous

Ans. 11: (b), (c) and (d)

Solution: For second order phase transition G is continuous $S=-\left(\frac{\partial G}{\partial T}\right)_P$ and $V=-\left(\frac{\partial G}{\partial p}\right)_S$ is continuous and $C_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ is finitely discontinuous .

Ans. 12: (c) and (d)

Solution: For second order phase transition G is continuous $S=-\left(\frac{\partial G}{\partial T}\right)_P$ and $V=-\left(\frac{\partial G}{\partial p}\right)_S$ is continuous and $C_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$ is finitely discontinuous

Ans. 13: (a), (b), (c) and (d).

Ans. 14: (a), (c) and (d)

Solution: $T_{\text{inversion}}=\frac{2a}{Rb}$, $T_{\text{Boyle}}=\frac{a}{Rb}$ and $T_{\text{critical}}=\frac{8a}{27bR}$

Ans. 15: (b) and (c)

Ans. 16: (b) and (d)

Solution: Joule-Thomson coefficient for ideal gas is zero

i.e., $\left(\frac{\partial T}{\partial P}\right)_H=0$

whereas for real gas it is given as

$$\mu=\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_P}\left(\frac{2a}{RT}-b\right)$$

a, b are Vander Waal's constant.

Ans. 17: (b) and (d)

Solution: When temperature of a gas is above a fixed temperature, known as critical temperature, the gas cannot be liquid whatever the pressure is applied.

If temperature of the gas is equal to or smaller than the critical temperature, then it can be liquefied.

Ans. 18: (a) and (c)

Solution: The fall of temperature is given as

$$dT = \frac{dP}{C_P}\left(\frac{2a}{RT} - b\right)$$

$$\Rightarrow \qquad T_i = \frac{2a}{Rb}$$

Thus, temperature $T > T_i$ then heating effect,

if temperature $T < T_i$ then cooling effect.

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